Dyes and Pigments 153 (2018) 137–143

Contents lists available at ScienceDirect

Dyes and Pigments

journal homepage: www.elsevier.com/locate/dyepig

Identification of yellow dyes in two wall coverings from the Palace Museum: Evidence for reconstitution of artifacts

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ARTICLE INFO

Keywords:
Glycosylated flavonols
HPLC-PDA-MS
SERS
Rhamnus
Wall coverings

ABSTRACT

Glycosylated flavonols were characterized in the extracts of *Rhamnus petiolaris* and *Rhamnus utilis*, by high performance liquid chromatography coupled with photo diode and mass spectrometric detectors (HPLC-PDA-MS). The main dye components are rhamnetin-3-*O*-rhamninoside for *R. petiolaris* and kaempferol-3-*O*-rhamninoside for *R. utilis*. Based on this information, the yellow dye used in the wall cloth in the Palace Museum can be identified as *R. petiolaris* or a closely related species. In the case of the wallpaper (which was under the wall cloth), the main flavonoid found was rutin, suggesting that it was dyed with buds of pagoda tree (*Sophora japonica*), a dye traditionally used in China. The results presented here provide valuable information in regard to reconstitution of the late Qing dynasty (1840–1912 AD) wall coverings. In addition to HPLC-PDA-MS analysis, surface enhanced Raman spectroscopy (SERS) was used to tentatively identify yellow dyes in the two historical artifacts. Only a 1 mm length of single fiber, obtained from each Qing dynasty sample, was needed for comparison with the SERS data of dye references. This ultra-sensitive method is suitable for situations where sampling is restricted to trace amounts.

1. Introduction

In 2015, the Palace Museum began renovation of the Hall of Mental Cultivation (Yangxin Dian) [1], in which eight emperors of the Qing dynasty lived and dealt with state affairs from the middle of the seventeenth century to the beginning of the twentieth century. This renovation project involves not only repairing the main building of Hall of Mental Cultivation, but also reconstitution of interior decorations and furnishings based on scientific research and traditional techniques. In one room, a study called *Changchun*, in the main building there is a wooden wall whose cloth covering has lilac (*Syringa* spp.) flower patterns (Fig. 1); the covering looks elegant but has many tears and is even missing pieces. It is also very interesting that a yellow wallpaper with brown patterns was discovered underneath; it was visible because the wall cloth was seriously damaged. We speculated that the wall cloth was pasted onto the surface of the wallpaper directly without removing the wallpaper, probably because the wallpaper was stuck strongly to the wall and was not easy to remove. To reconstitute either of the two wall coverings it is necessary to understand which materials, e.g., fibers, dyes and adhesives were used to produce those coverings.

Dye analysis of historical textiles and paintings can reveal clues about when and where the objects were made. For example, chromatographic profiling of carminic acid and its derivatives, along with a statistical approach, has been successfully used to distinguish between Polish cochineal (*Porphyrophora polonica*) and American cochineal (*Dactylopius coccus*) in historical textiles [2], which were endemic in Europe and South America, respectively, around the sixteenth century. Moreover, Direct Red 23 was found in an Uzbek ceremonial coat, indicating that the creation date of the garment was early twentieth century or later [3], because this early synthetic dye was first reported in 1900. On the other hand, the determination of dye types helps museum curators and conservators control exhibition time and lighting in order to minimize fading of the colorful artifacts.

During the past decade, several tools have been applied to dye analysis, the most impressive of which are high performance liquid chromatography coupled with photodiode and mass spectrometric detection (HPLC-PDA-MS) [4] and surface enhanced Raman spectroscopy (SERS) [5].

HPLC-PDA-MS is a useful tool that can provide information not only about the absorption spectra, but also the molecular masses of each component and their fragment ions. This tool has been widely used to identify various species of natural dyes including anthraquinones,

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https://doi.org/10.1016/j.dyepig.2018.01.057
Received 9 November 2017; Received in revised form 8 January 2018; Accepted 30 January 2018
Available online 03 February 2018

Fig. 1. A wall cloth with lilac (*Syringa* spp.) flower patterns was found in the *Changshun* study of the Hall of Mental Cultivation. Beneath the damaged wall cloth was found a yellow wallpaper with brown figures. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

flavonoids, alkaloids, tannins and indigoids [6], as well as many early synthetic dyes [7]. With advantage of mild extraction methods that preserve the glycosidic linkages of flavonoids, HPLC-PDA-MS enable researchers to determine original vegetable or animal dyestuffs used to color ancient objects. For example, Zhang et al. [8] characterized two major types of yellow dyes in Pre-Columbian Andean textiles using formic acid in methanol to extract the dyes from the textile fibers. During the past decade, oxalic acid in methanol/acetone/water [9] or in pyridine/water [10], and trifluoroacetic acid in methanol/water [11] have also been used to extract dyes from archaeological and historical textiles. More recently, instead of the acid extraction methods, an alkaline extraction technique based on ammonia-EDTA has been applied to characterize two insect dyes from dyed yarns and lake pigments by HPLC-HRMS, this has proved to be an effective method for extraction of glycosylated anthraquinones [12].

HPLC analysis for dye identification usually requires 0.2–0.5 mg of a sample, which is really a quite small amount for most objects. However, this amount of sample is relatively large for a very tiny object. Fortunately, the use of surface enhanced Raman spectroscopy (SERS), which is an ultra-sensitive technique that has been employed for detecting coloring matters in ancient artifacts such as textiles and paintings, can overcome this difficultly in some cases. Leona and his coworkers [13] detected alizarin in a single, 1-mm long wool fiber from a sixteenth-century tapestry, treated with HF vapor and silver colloid. The amount of sample needed for SERS examination is at least 50 times less than that needed for HPLC analysis. Furthermore, SERS can sometimes be used on intact objects, without the need for removal of analytical samples [14]. Nevertheless, it should be noted that because the dye components are not separated using the SERS technique, as they are by HPLC, it is often not possible to identify the original source (plant or animal) of the dye, as most natural dyes contain a mixture of structurally-related components.

In the present study, the yellow dyes found in two wall coverings of the Palace Museum were characterized by both HPLC-PDA-MS, which revealed the presence of flavonoid dyes and some synthetic dyes, and SERS, which provided partial confirmation of the HPLC-PDA-MS results.

Since this paper focused on dye analysis, identification of fibers and adhesives for the two wall coverings is not described.

2. Experimental

2.1. Materials

Immature fruits of *Rhamnus petiolaris* (more commonly referred to as Turkish berries) were obtained from Prof. Richard Laursen, Boston University, USA. Green fruits of *Rhamnus utilis*, so-call Chinese berries, were collected at the Hangzhou Botanical Garden and then dried at ambient temperature. Fresh buds of the pagoda tree (*Sophora japonica*) were collected at the China National Silk Museum, then immediately heated in oven at 110 °C for half an hour to inactivate glycolytic enzymes [15]. Rue (*Ruta graveolens*) leaves were obtained from Dr. Chika Mouri, Smithsonian Institution, USA.

HPLC-grade Methanol and acetonitrile were purchased from Merck (Germany), LC-MS-grade formic acid from Fisher Scientific (USA), HPLC-grade pyridine from ANPEL CNW (China), and oxalic acid (≥98%) from Acros Organics (USA). Sodium citrate tribasic dihydrate (≥99.5%) and silver nitrate (99.99%) were purchased from Sigma-Aldrich (USA). Ultra-pure water (18.2 MΩ) was obtained using a Millipore Reference purification system (France).

Rhamnetin (≥99%) and rhamnazin (≥99%) were purchased from Sigma-Aldrich (USA); rutin (≥98%), isorhamnetin (≥98%), kaempferol (≥98%) and quercetin (≥98%) were purchased from Aladdin (China). All dye standards were dissolved in methanol/water (1:1) at a concentration of 2 mg/mL and then diluted with the same solvent to a final concentration of 10^{-5} M. Five microliters of the solution was directly injected onto the HPLC column; 0.25 μL of the solution was directly examined by SERS.

2.2. Extraction of plant material

Dried plants were crushed and powdered using a pestle and mortar, and then 2 mg of the powder was extracted with 1 mL of methanol/water (1:1) at 70 °C for 30 min. The extracts were subsequently centrifuged at 14000 × g for 5 min, 10 μL of the supernatant was mixed with 990 μL of methanol/water (1:1) and then the diluted extract was directly analyzed by HPLC and SERS.

2.3. Extraction of dyes for HPLC-PDA-MS

Dyes were extracted from a piece of yarn (about 0.2 mg) from the wall cloth and from a small fragment (1 mm × 1 mm) of the wall paper, each in 200 μL of a solution of pyridine/water/0.5 M oxalic acid in water (95/95/10) heated at 90 °C in a heating block for 30 min. The extracts were immediately transferred into a 1.5-mL centrifuge tube (Eppendorf, Germany) and evaporated to dryness under a stream of nitrogen. Subsequently, the residue from each extract was dissolved in 50 μL of methanol/water (1:1) and centrifuged at 14000 × g for 5 min, after which 30 μL of the supernatant was transferred to a 200-μL microvial, from which 20 μL was applied to an HPLC column.

2.4. Preparation of silver colloids

Silver colloids were prepared following the Lee-Meisel procedure [16] by reduction of silver nitrate with sodium citrate. All glassware was cleaned with aqua regia solution and rinsed with ultrapure water and methanol. The absorption maximum of the colloid is observed at 417 nm (Fig. S1a), as measured with a Cary 50 spectrophotometer (Varian, USA). A Sigma 300 FE-SEM (Zeiss, Germany) measurement shows that the silver colloids consist of mostly spherical nanoparticles with diameters ranging from 35 to 75 nm (Fig. S1b).

Concentration of silver colloids to produce silver colloidal paste was carried out following the method of Idone et al. [17]. Aliquots (40-mL) of silver colloids were centrifuged at 8000 rpm for 6 min, the supernatant was discarded and an additional 40-mL aliquot of silver colloid was added into the centrifuge tube. Subsequently, the centrifugation