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Characterization of weld (*Reseda luteola* L.) and spurge flax (*Daphne gnidium* L.) by high-performance liquid chromatography–diode array detection–mass spectrometry in Arraiolos historical textiles

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ABSTRACT

The natural dyes, and dye sources, in two seventeenth century Arraiolos carpets from the National Museum of Machado de Castro were analysed by high-performance liquid chromatography with UV–vis diode array detection (HPLC–DAD) and HPLC–mass spectrometry (LC–MS). Weld (*Reseda luteola* L.), indigo and spurge flax (*Daphne gnidium* L.) were found to be the dye sources, in agreement with original dyeing recipes collected during the nineteenth century. In order to fully characterize the plant sources, LC–MS conditions were optimized with plant extracts and the chromatographic separation and mass detection were enhanced. Extraction of the dyes, in the Arraiolos carpet samples, was performed using mild conditions that avoid glycoside decomposition. For the blues a dimethylformamide solution proved to be efficient for indigotin recovery. For all the other colours, an improved mild extraction method (with oxalic acid, methanol, acetone and water) was used, enabling to obtain the full dye source fingerprint, namely the flavonoid glycosides in the yellow dyes.

1. Introduction

The Arraiolos' carpets, from the town of the same name, are an important and unique Portuguese textile tradition. The oldest pieces display a great resemblance with Persian carpets in which the decoration patterns and the role played by symmetry in the final design concern [1]. Their origin is rather obscure, but it is known that by the seventeenth century Arraiolos, a town in the South of Portugal (Alentejo), was an important production center [1]. The materials used on the manufacture were locally provided, like sheep wool, or were imported, like indigo or brazilwood dyes [1–4]. During the seventeenth century, the colour palette of these textiles was based on six colours, which are described in nineteenth century dyeing recipes, collected in the town of Arraiolos [5]. The blue colour was obtained with indigo; the reds with brazilwood or brazilwood and spurge flax; yellows with weld or weld and brazilwood; the greens were dyed with indigo and weld; the purple was dyed with brazilwood, and the browns with brown natural wool dyed with spurge flax [3,6], Fig. 1.

Illustrative of this palette are two Arraiolos carpets (T763 and T764) from the National Museum of Machado de Castro (MNMC), dated from the seventeenth century, presenting a design where outstands floral (palm tree leaves and lotus flowers) and Herati Persian (cloud motif) motifs. The medallion carpet (Fig. 2) is one of the most important examples of the Persian influence in Arraiolos carpets' design [1]. The colours present in both carpets are very similar—yellow, blue, green, cream and brown. In earlier descriptions, a red colour was mentioned in some motifs, which is not observed at least since 1973 [1].

The fingerprint of the dyes used, the establishment of their biological source, how they have been prepared, – all these facts and others – can provide important information as to where, when, and how these historical textiles were made [7]. Thus, it is crucial to fully extract the information that can lead to the identification of a particular plant or other dyestuff used to colour a textile. Since most textiles are mordanted with metal ions (for example Al^{3+}), the extracting solution must be able to disrupt the dye–metal complex.

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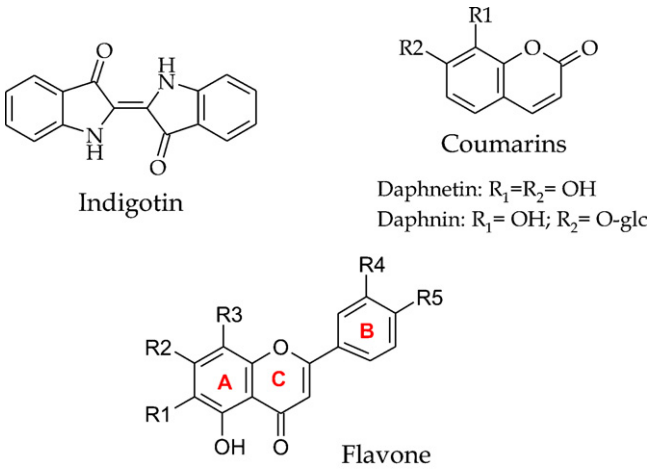

Fig. 1. Chemical structures of indigotin and major compounds of weld and spurge flax.

Fig. 2. Arraiolos carpet T764 (middle-17th century) from the MNMC.

Until recently, historical dyes have been extracted with solutions based in strong acids like HCl [8,9], able to disrupt the dye from the fibres and decompose the dye–metal complex, enabling the dye recovery. However the strong acids decompose many flavonoid glycosides to their parent aglycons, resulting in information loss on the dye source, which is particularly relevant in the case of flavonoid yellows. The use of mild reagents, like acid formic, oxalic acid or EDTA [10,11] enable an efficient dye extraction while preserving the glycoside linkages and thus, more information on the dye source can be obtained. In order to process this information, it is necessary to characterize thoroughly extracts of known yellow dyeing sources.

In the present study HPLC–DAD and LC–MS were used for qualitative characterization of the expected yellow dyeing sources (weld and spurge flax) prior to the characterization of samples from Arraiolos carpets. The importance of the information from the parent ion mass and fragmentation patterns obtained with MS and the correlation with the UV–vis absorption spectra obtained with DAD for a full characterization of yellow raw materials and yellow Arraiolos samples was demonstrated. Complementary to the dyes identification, it was also important to confirm the reliability of the Arraiolos dyeing recipes by analysing and characterizing the mordants by inductively coupled plasma with atomic emission spectrometry (ICP-AES).

2. Experimental

2.1. Chemicals

Aluminium, multielementar (Cd, Cr, Cu, Fe, Mn, Ni, Pb, Sb, Sn, and Zn) standards and nitric acid for mordant analysis were inductively coupled plasma (ICP) grade or equivalent. For all other experiments, spectroscopic or equivalent grade solvents and millipore filtered water were used (Millipore Simplicity Simpak 2, $R = 18.2\ M\Omega\ cm$, USA).

Flavonoid standards for HPLC were purchased from Extrasynthèse (Genay, France). Dye plants were purchased from Zecchi (Florence, Italy), weld (*Reseda luteola* L.); Dr. Alessandro Bizzarri (Florence, Italy), brazilwood (*Caesalpinia brasiliensis* L.); Kremer (Aichstetten, Germany), indigo (*Indigofera tinctoria*). Spurge flax (*Daphne gnidium* L.) was cropped near Carcavelos beach in February, May and June 2007 (Lisbon, Portugal). All other reagents were of analytical grade.

2.2. Sampling and extraction dyes methods

Three samples were collected from each colour and area – main border and the field, – from both carpets. Each sample weighted *ca.* 0.2–0.5 mg. A total of 82 samples (42 from T763 and 40 from T764) were selected for HPLC–DAD analysis: 20 yellow (8 light yellow, 8 medium yellow and 4 dark yellow), 7 cream, 28 blue (14 light blue and 14 dark blue), 16 green (4 light green and 12 dark green) and 11 brown. Furthermore, 5 samples were also analysed with LC–MS (2 medium yellow and 3 dark yellow).

Oxalic acid extraction for textile samples was carried out as follows: a small sample of thread was extracted with a 400 μL solution of oxalic acid (0.2 M):methanol:acetone:water (0.1:3:3:4, v/v) in 1.5 mL eppendorfs for 30 min in a 60 °C water bath, with constant agitation [11,12].

Dimethylformamide (*DMF*) *extraction* (only for blue and green samples) was carried out as follows: a small sample of thread was extracted with 400 μL of DMF in the same conditions for oxalic acid extraction [13]. After extraction, each extract was dried in a vacuum system, where the resulting dry residues were reconstituted with 50 μL methanol:water (1:1, v/v).

These two extraction methods were also applied in the historic reconstructions of textile samples.