



Methodology for the Identification of Organic Dyes Used in Tapestries

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Abstract

For dyeing yarns used in the production of tapestries, one of the most important source during the centuries was the root of madder (*Rubia tinctorum* L.). On many tapestries, there is a widespread state of decay in charge of yarn dyed in red, violet and yellow. This phenomenon may be due to total destruction of dye molecules, presence of alteration products trapped in the fibers or mechanical alterations of the yarn. Madder root, for example, contains a large number of compounds characterized by anthraquinone structures, which give to the yarn a red hue. During the dyeing process, however, also other types of molecules (not necessarily anthraquinones), present in the matrix, are fixed on the yarn and, probably, these are also involved in the degradation process. Experimentally it is in fact observed that some compounds show a faster degradation than the others. In order to establish an appropriate restoration, it is necessary to identify all the compounds involved and then clarify the mechanisms of degradation. In this work, it has carried out extraction of dyes from textile fibers coming from some tapestries in the Vatican Museums; extracts has been analysed by High Performance Thin Layer Chromatography (HPTLC), Proton Nuclear Magnetic Resonance (¹H-NMR) and ElectroSpray Ionization – Mass Spectrometry (ESI-MS). The compounds thus isolated has been then compared with those extracted from madder root and from samples of dyed yarn according to the old recipes and subjected to artificial aging.

Introduction

In Raphael's tapestries, as in other tapestries in general, is noticeable a state of deterioration and discoloration of the dyes used in the dyeing of yarn, especially for the colours yellow, red and purple. The back of the tapestries (the "verso") apparently is not subject to decay. In this part this phenomenon is apparently not active or in an initial step. The degradation of the colour of the fibers visible on the right of the tapestry may be due to the total destruction of the dye molecules, the presence of alteration products of these molecules were trapped in the fibers. It may have occurred mechanical alterations of the surface of the yarn. If it considers the madder root, it contains a large number of compounds characterized by an anthraquinone structure, which give to the yarn the red hue. During the dyeing process, however, also other types of molecules (not necessarily anthraquinones), present in the matrix, are fixed on the yarn. These substances may be involved in the aging process and their participation in the processes of degradation or function is currently under investigation. The aim of this work is to develop a methodology for the identification of dye molecules and not, fixed on tapestries, and thus probably involved in the mechanisms of degradation.

Materials & Methods

Madder roots purchased from Kremer Pigmente GmbH & Co. KG have been used in order to obtain the dye bath and a total extract. Firstly, this extract has been studied through liquid chromatography and both ¹H-NMR. Fractions obtained were compared with extracts from historical yarns and "contemporary textiles" dyed according to original recipes. This comparison has been carried out through HPTLC, which allows to focus on the most important compounds, present in all these samples. These samples have been then analysed with TLC and ESI-MS in both positive and negative mode.

Results

The HPTLC analysis were performed on the fractions from madder's extract and those from historical and contemporary fibers. In this way, it highlighted which bands were present in all the samples. For this reason, these samples were solubilized in a 1:1 mixture of acetonitrile and 0.3% formic acid in water and then analysed in ESI-MS in both positive and negative mode. With this technique, it has been possible to draw a structural profile of the compounds. Specifically, it has been recognized an hydroxy hydroxymethyl anthraquinone and a glycosyl asperulosidic acid.

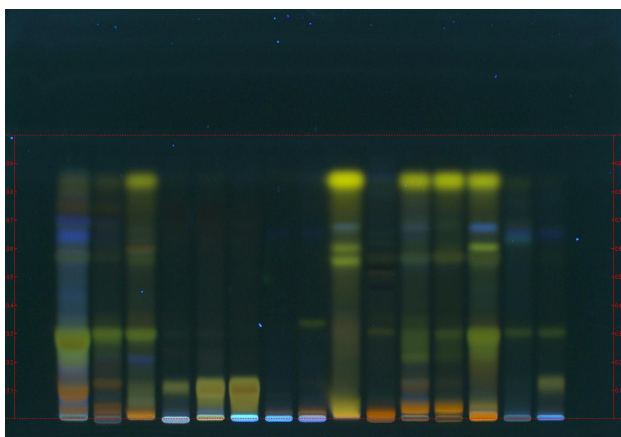


Fig. 1; HPTLC of most important fractions from Madder's root.

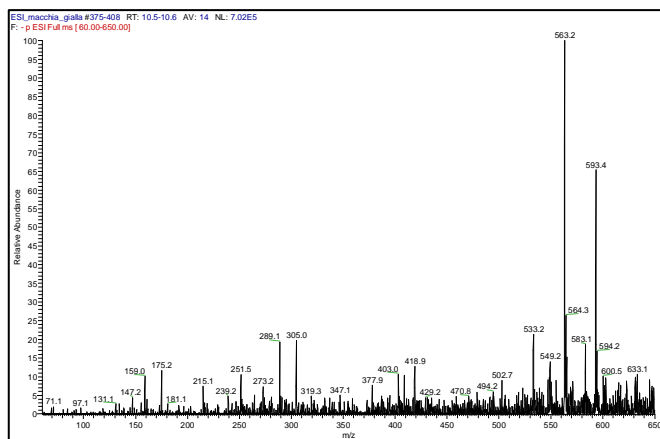


Fig. 2; full mass spectrum of yellow band.

Conclusions

The liquid chromatography and subsequent NMR, ESI-MS and ESI-MS/MS analysis have identified, in addition to the already known purpurin and alizarin, some of the many other compounds present in the madder's root, extracted during the dye processes and probably fixed on fiber. This phenomenon will be clarified in order to understand the importance of these compounds in the degradation processes. It is carrying out the full identification of all the compounds revealed by HPTLC. In order to improve the number of information obtainable from the historical textiles, it will be investigated and employed new techniques for a soft extraction of the dye from the fibers. As a further development, the study of the mechanisms and modes of degradation of the colouring substances and textile fibers will be approached, in order to design new ways of restoration of tapestries and other textiles.

References

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