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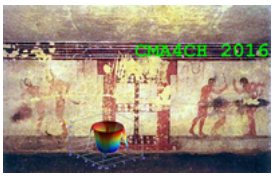

Clarification of Chemical Composition of American Cochineal, in Order to Evaluate the Applicability of Statistical Analysis for Distinguishing Different Species of Cochineal

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Abstract

Cochineal dyes are representing in the last years one of the more interesting challenge for researchers in conservation field. Widely used during the century, object of investigation in several studies, mainly because of several compounds unknown. Recent studies have been focused on the elucidation of these unknown structures, moved by the idea that, in studying artworks and dyes employed, it is not possible to look at few molecules, thought as responsible for the colour, as "marker" molecules, easily detectable, to discriminate the matrix employed. However, this approach is not sufficient if we need to preserve the artwork, understand which matrix has been employed the provenance and, at least, hypothesize the degradation path. Furthermore, in order to clarify the provenance of the materials, statistical analysis seems to facilitate the classification of cochineal species found in the historical samples.

In this paper, preliminary results of the new mild extraction methodology are presented [4]. The characterization of compounds was performed through HPLC-MS (in SIM mode and MRM), confirmed the presence of O-glycosyl anthraquinones, never extracted before in this matrix, allowing the approach to future statistical analysis with a more complete chemical overview.

Introduction

The insects employed in dyeing processes, paintings, but also in food and pharmaceuticals industries nowadays are the Hemiptera, belonging to the Coccoidea superfamily.

Cochineal, such as other insect dyes, represents one of the most precious dye in history. Even if it was not easy to find and required a complex dyeing process, due to its wonderful, brilliant and enduring colour, this dye was extremely requested. Because of these difficulties in recovering the insect, its price was expensive and, for this reason, it was used only for prestigious manufactures (1; 2). Symbol of wealth and power, until the 16th century, the major sources were Polish (*Porphyrophora polonica* L.) and Armenian cochineal (*Porphyrophora hamelii* B.) for what concern the cochineals, and insects of lac (Kerria lacca) and kermes (*Kermes vermilio* P.), as other insects employed. A threshold of complete change is represented by the year 1523. A new species of cochineal came from Mexico: the *Dactylopius coccus* O. G. Costa (1, 2). The rapid success of this new species was due to its higher colorant content. In fact, as reported by Serrano, it contains 10-12 times more colorant than kermes [Serrano et al., 2015]; that means that for the same dye bath, a very minor amount of insects was required, resulting in price falling (1, 2). This fact was fundamental for the next demand of dyestuff in Europe and this insect become the most imported by Spanish. Even if it seems to be sure that in Europe, it replaced totally Armenian and Polish cochineal, in few decades, the same information could not be applied also for Asian trade, for the few historical proofs (2). The capability of distinguishing between American, Polish and Armenian cochineal can result fundamental to trace the historical trades and extend the knowledge of economic and historical data of the past.

Wouters and Verhecken suggest a distinction between the different species of insects, based on the visual examination and quantification of representative compounds detected with a HPLC-UV-vis

detector (3). Furthermore, several works have been conducted based on the clarification of unknown secondary compounds (4-6). In addition, PLS-DA models of the chromatographic data seems to facilitate the classification of cochineal species found in the historical samples (2). The aim of the application of the new ammonia extraction technique is to evaluate the capability of extracting glycosides from cochineal dyed yarns and lake pigments and, at the same time, understand if different species of C- and O-glycosides can be extract, with a milder methodology (7).

Materials & Methods

Cochineal, 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 LC and both ^{1}H-NMR. Furthermore, the extracts have been analysed through HPLC-MS.

Results

The characterization of compounds was performed through HPLC-MS (in SIM mode and MRM), ^{1}H-NMR, ESI-MS experiments in a first step. In addition, 2D NMR analysis confirmed the presence of O-glycosyl anthraquinones, extracted and conserved with this mild approach and MRM transition allowed to discriminate between the several glycosyl compounds. Particularly interesting can be considered the presence of glycosil compounds, identified before only in Polish cochineal.[1, 2, 3].

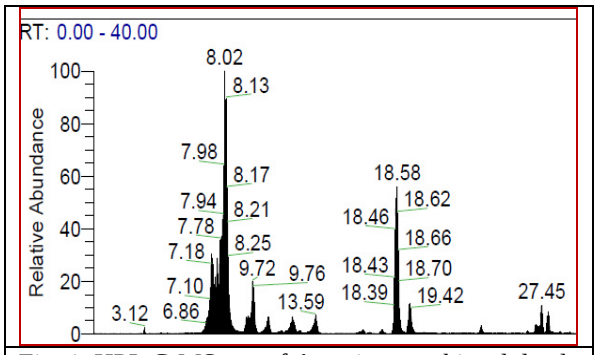

Fig. 1. HPL C-MS run of American cochineal dyed yarn extracts.

Conclusions

Taking into account the results obtained, it is possible to affirm that the ammonia extraction protocol can be successfully applied to cochineal dyed yarns and lake pigments, with slight modifications. The mild character of this extraction has led to the identification of different glycosyl compounds. In particular, di-glycosides and monoglycoside of kermesic and flavokermesic acid, mentioned before only for Polish cochineal, has been recovered also in American cochineal dyed yarn and lake pigments.

References

1) D. Cardon, *Le Monde des Teintures Naturelles*, Edition Belin, Paris, 2014.
2) A. Serrano, A. Van Den Doel, M. Van Bommel, J. Hallett, I. Joosten, K. J. Van Den Berg, Investigation of crimson-dyed fibres for a new approach on the characterization of cochineal and kermes dyes in historical textiles, *Anal. Chim. Acta*, 897, 2015, 116-127.
3) Wouters J., Verhecken A., The coccid insect dyes: hplc and computerized diode array analysis of dyed yarns, *Studies in Conservation*, 34(4), 1989, 189–200.
4) K. Stathopoulou, L. Valianou, A.L. Skaltsounis,I. Karapanagiotis,P. Magiatis, Structure elucidation and chromatographic identification of anthraquinone components of cochineal (Dactylopius coccus) detected in historical objects, *Anal. Chim. Acta*, 804, 2013, 264-72.
5) K. Lech , K. Witkoś, B. Wileńska B., M. Jarosz, Identification of unknown colorants in pre-Columbian textiles dyed with American cochineal (Dactylopius coccus Costa) using high-performance liquid chromatography and tandem mass spectrometry, *Anal Bioanal Chem*, 407, 2015, 855–867.
6) K. Lech, M. Jarosz, Identification of Polish cochineal (Porphyrophora polonica L.) in historical textiles by high-performance liquid chromatography coupled with spectrophotometric and tandem mass spectrometric detection, *Anal Bioanal Chem*, 408, 2016, 3349–3358.
7) L. Lombardi, I. Serafini, M. Guiso, F. Sciubba, A. Bianco, A new approach to the mild extraction of madder dyes from lake and textile, *Microchem. J.*, 126, 2016, 373–380.