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A diagnostic study on *folium* and *orchil* dyes with non-invasive and micro-destructive methods

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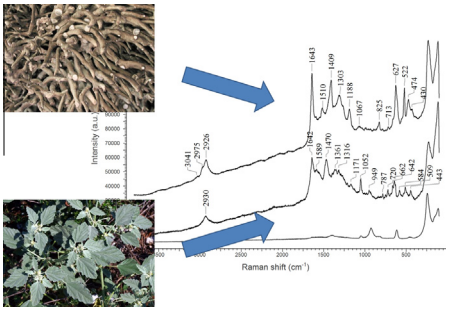
HIGHLIGHTS

- Non-invasive and micro-invasive techniques used for folium/orchil identification.
- Diagnostic information on these dyes strongly increased.
- Historical reconstructions performed in order to have reliable standards.
- Evidence that bromine is not a key marker exclusive for Tyrian purple.
- Most folium spectral features presented for the first time in a scientific work.

GRAPHICAL ABSTRACT



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ABSTRACT

Folium and *orchil* are dyes of vegetal origin. Folium is obtained from *Chrozophora tinctoria* (L.) A. Juss., whereas orchil is obtained from *Roccella* and other genera of lichens. These dyes were used in the past to impart purple hue to paintings and textiles as substitutes for the more prised Tyrian purple dye, obtained from shellfish. Despite several citations in ancient technical treatises dating back at least to the Greek-Roman age, the identification of these dyes in artworks is rare. In the case of folium, an additional drawback is that its composition is presently unknown.

In this work different non-invasive (FT-IR, FT-Raman, fibre optic reflectance spectrophotometry, spectrofluorimetry, X-ray fluorescence spectrometry) and micro-invasive (surface enhanced Raman spectroscopy, matrix assisted laser desorption ionisation-time of flight-mass spectrometry, inductively coupled plasma-mass spectrometry) techniques were used in order to increase the diagnostic information available on these dyes. Measurements were carried out on the dyes extracted from raw materials and on painted or dyed parchments. The possibility to distinguish between folium and orchil by chemical analysis is discussed.

Introduction

The names *folium* and *orchil* are used today to indicate two kinds of dyes of vegetal origin, obtained from *Chrozophora tinctoria* (L.) A. Juss. and from several genera of lichens, respectively. These

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dyes have been in use for a long time to impart purple hue to artworks, either dyed or painted; they were in fact mostly used as substitutes for the more priced Tyrian purple, the famous dye obtained from shellfish. For several centuries, though, folium and orchil were hardly considered as different materials, as the historical terminology used for their description in the technical and artistic literature was confusing. In many medieval manuscripts, similar names were given to lichen dyes and to dyes obtained from *Chrozophora* species. As an example, lichens of *Roccella* species were also known as *tournesol* which is a traditional name used for *Chrozophora tinctoria* (L.) A. Juss. plant. It is only in the 19th century that ambiguity was resolved [1,2] and the different origin of these dyes was ascertained.

The term *orchil* refers primarily to red and purple dyes obtained from various lichen species upon fermentation in ammonia. Although the most renowned orchil-producing lichen species are those of *Roccella* genus (e.g. *Roccella tinctoria*, *Roccella montagnei*, *Roccella fuciformis*, etc.), *Dendrographa*, *Diploschistes*, *Evernia*, *Lasallia*, *Lecanora*, *Ochrolechia*, *Parmelia*, *Pertusaria*, *Umbilicaria* and *Variolaria* genera are other sources of orchil [3–5]. *Orchil* has been intended as a general name for purple lichen dyes at least since the end of 19th century. Nevertheless, in the past this name (and the dialectic variants *archil*, *orchall*, *orseille*, *oricello*, etc.) referred mainly to the dye obtained from *Roccella* species, while different names were used for regional varieties: *cudbear* was the name given to a purple dye obtained from *Lecanora* species widely common in Scotland (e.g. *Ochrolechia tartarea*), while in Scandinavia a similar dye, known as *korkje*, was extracted also from *Lasallia* and *Umbilicaria* lichens; another purple dye, obtained from lichen species living in Central France, was known as *parelle*. Purple dyes from lichens were in use at least since Greek-Roman times: literary citations from Theophrastus, Dioskurides and Pliny the Elder are known [6,7] which highlight their role as a substitute of Tyrian purple in dyeing. Pliny the Elder, in particular, suggested that orchil could be used to dye wool textiles as a background where a small amount of Tyrian purple was subsequently applied, a procedure known as top-dyeing [8]. Moreover, several recipes in the Greek manuscript known as *Stockholm Papyrus* (3rd century A.D.) recommended the use of dyes obtained from lichens to imitate purple [9]. As for painting, medieval treatises cited orchil as a suitable colourant, such as the manuscript *Ut auro scribatur* [10] where its use is suggested as a paint (not as a dye) to impart purple colour to parchment in purple codices. The composition of orchil, though complex, has been elucidated and reviewed in several studies [11,12]. Lichens contain depsides and depsidones which are precursors of the dye. Precursors can change from species to species but, in the case of purple-generating species, the main precursors are erythrin, evernic acid, gyrophoric acid and lecanoric acid; after extraction, these compounds are hydrolysed to orsellinic acid and decarboxylated to colourless orcinol, which is oxidised to orcein upon introduction of ammonia. Orcein is actually made up of a mixture of phenoxazone derivatives such as hydroxyorceins, amino-orceins and amino-orceimines.

Folium is extracted from *Chrozophora tinctoria* (L.) A. Juss, a plant known as *turnsole* or *morella*, native of coastal Mediterranean countries. Interestingly, the German name for turnsole has been for long *lackmuskraut*, a term meaning litmus-herb, where litmus is another dye produced from *Roccella tinctoria* lichens differing from orchil in reason of its polymeric structure. Literary citations concerning the use of *folium* in artworks are found later than those concerning orchil. The first recipes for the preparation of folium date back to 11th century A.D. but its use in painting can be probably referred to the early Middle Ages [13] since it is cited in the 9th century *Mappae Clavicula* treatise [14]. However, it is highly probable that turnsole was already in use in Roman times. Pliny the Elder [8] in his *Naturalis historia*, book XXII, chapter 29, mentions in fact a vegetal species which he called *Heliotropium tricoccum*. This may indicate the presence of three cells in the capsule of the plant, as the characteristic tri-lobed fruits yielding folium dye. Among others, Theophilus in his famous *De diversis artibus* treatise [15] and the anonymous author of the *De arte illuminandi* treatise [16] highlighted the fact that this plant can produce a red, violet or blue dye if berries are extracted respectively with an acid, neutral or alkaline solution: the so-called *folium rubeum*, *folium purpureum* and *folium saphireum*. The name folium, however, is historically referred to the purple-violet phase. The scientific knowledge on the composition of folium is relatively scarce if compared to orchil. Early studies [17] suggested that, according to its properties of changing colour on varying pH, folium could contain anthocyanin compounds. Other studies [18–20] suggested instead the similarity between folium and orchil from a compositional point of view. Guineau showed results from time-of-flight mass spectrometry (ToF-MS) analysis in his detailed historical and diagnostic study [13], which highlighted the presence of orcinol, a compound also present in lichen dyes.

Identifications of folium and orchil on artworks are rare, in particular when non-invasive analyses are considered. Orchil was identified by Clementi et al. [21,22] by means of fluorescence spectroscopy in some Renaissance tapestries and in purple details of the miniatures of the *Book of Kells* [23], a famous 8th–9th century A.D. manuscript. The same authors identified orchil on the parchment of the *Bible de Théodulfe* (9th century) using fluorescence spectroscopy and subtracted shifted Raman spectroscopy, [24] and Eveno et al. [25] gained a similar identification by HPLC. Aceto et al. [26] analysed the parchment of the *Codex Brixianus*, a 6th century A.D. purple manuscript, using UV–visible diffuse reflectance spectrophotometry, spectrofluorimetry and X-ray fluorescence spectrometry and suggested that both orchil and folium could be present. Recently Bicchieri [27] identified orchil by means of UV–visible diffuse reflectance spectrophotometry on the parchment of the precious *Codex Rossanensis*, another 6th century A.D. purple manuscript. Finally, the identification of litmus was carried out by Baraldi et al. [28] with Raman spectroscopy on a 17th century painted table. As regards folium, the number of identifications is very limited since it can be circumscribed to the pioneering work by Guineau [13] in which the author identified the dye in some 9th–11th century manuscripts by means of UV–visible diffuse reflectance spectrophotometry, to the tentative identification on the *Sinope Gospels* (a 6th century A.D. purple manuscript) by means of GC–MS by Thomas and Flieder [18] and to the tentative attribution to folium of blue areas in the de Brécy *Madonna and Child* tondo painting, analysed with FT-Raman spectroscopy by Edwards and Benoy [29].

From the artistic point of view, the use of folium and orchil in painting is certainly suitable for obtaining a range of hues from red to blue through purple, as described in several medieval artistic treatises. Therefore, despite the very low number of identifications on artworks, the number of instances in which these dyes could have been used is possibly much larger than the number of actual identifications. Moreover, the overview on the literature reported above highlights that the diagnostic information concerning these dyes is very limited or, as in the case of folium, almost absent. In the present work we aim to increase the diagnostic information available for the detection of folium and orchil by means of the spectroscopic techniques that are normally used in the analysis of painted artworks, with particular concern to illuminated manuscripts; therefore in this study folium and orchil have been subjected to a deep analytical investigation with a particular focus on the use of a non-invasive or a micro-invasive approach. The following non-invasive techniques were considered: Fourier transform Raman spectroscopy (FT-Raman), Fourier transform infrared spectrophotometry (FT-IR) both in transmission mode and in attenuated total reflection (ATR) mode, spectrofluorimetry,