Lichen Biodeterioration of the Convento de la Peregrina, Sahagún, Spain

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ABSTRACT: Lichen encrustations from *Diploschistes scruposus* involved in the biodeterioration of the 13th Century Convento de la Peregrina in Sahagún Spain, have been analyzed using Raman spectroscopy. The vibrational spectra are characteristic of calcium oxalate monohydrate, β-carotene, chlorophyll, and *para*-depside phenolic acids such as atranorin, lecanoric acid, and diploschistesic acid. The destructive colonization of the monumental stonework is highlighted and evidence presented for deleterious lichen invasion of the wall paintings inside the Convent. © 1999 John Wiley & Sons, Inc. Biospectroscopy 5: 47–52, 1999

Keywords: lichen; biodeterioration; Raman spectroscopy; wall paintings; pigments

INTRODUCTION

The biodeterioration of ancient monuments by lichens is often ascribed to the production of encrustations at their substratal interfaces formed from the chemical reaction of metabolic by-products with minerals in the stone.[1–4] Extensive erosion of the substratal material is often observed, particularly with aggressive colonizations by lichen species which produce secretions of oxalic acid from the mycobiont; in the presence of calcareous substrata, significant corrosion and pitting can occur.[5,6]

There is strong evidence that recent environmental changes have been conducive to increased invasions by aggressive lichens such as *Dirina, Lecanora,* and *Acarospora;* recent Raman spectroscopic studies from our laboratory have drawn attention to the different strategies which can be adopted by lichens in their colonization of a range of substrata under different climatic or geographical conditions.[7–9] In some cases, according to the chemical or geological nature of the substratum, other products can be incorporated into the encrustation or physically entrapped in the lichen growths; the physical incorporation of particulate calcite in calcareous *Dirina* encrustations[5,6] and manganese and copper oxalates in *Pertusaria* growths on manganese and copper-rich rocks have been reported.[10,11]

Whereas lichen biodeterioration of natural stone outcrops has long been recognized as a primary source of soil formation in a geological time frame, the disfigurement of man-made monuments through chemical attack by lichen metabolic by-products has become apparent in recent years.[2] The obliteration of wall paintings and frescoes by invasive lichen growths, often resulting in detachment of the painted layers from the substrata, has been the subject of several spectroscopic investigations.[5,6,12,13] In recent work from our laboratory,[14] the identification and characterization of mineral pigments used in the medieval wall paintings at the Convento de la Peregrina in Sahagún, Spain (Fig. 1), was accomplished using Raman spectroscopy. This important medieval

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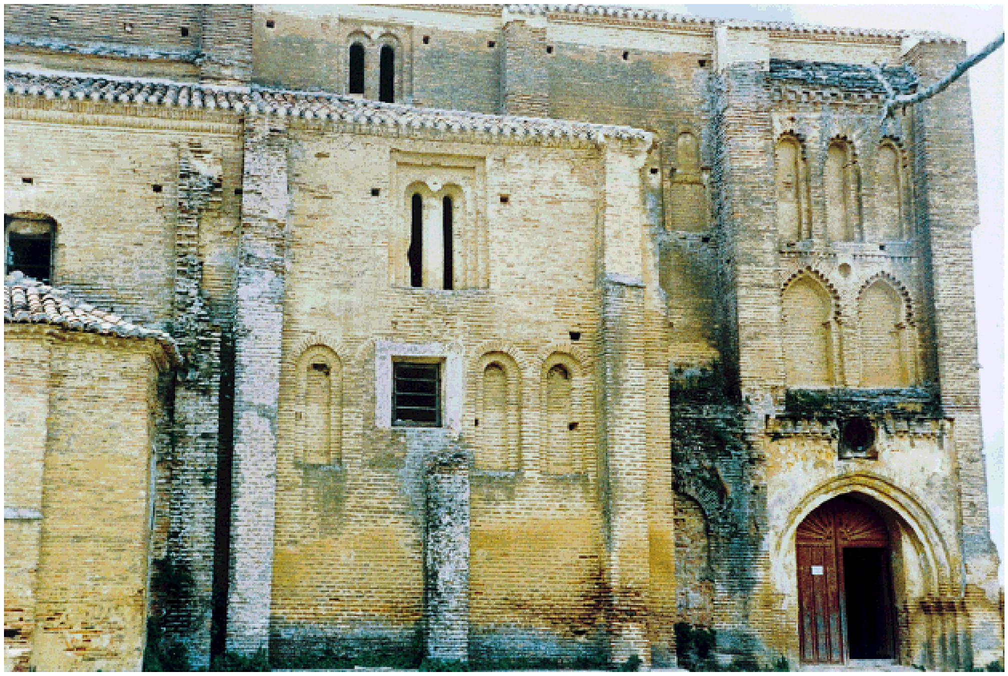

Figure 1. Convento de la Peregrina, Sahagún, Léon, Spain. The extensive white coverage of the outer walls to the left of the entrance door due to colonies of *Diploschistes scruposus* is significant. The unglazed window apertures should also be noted.

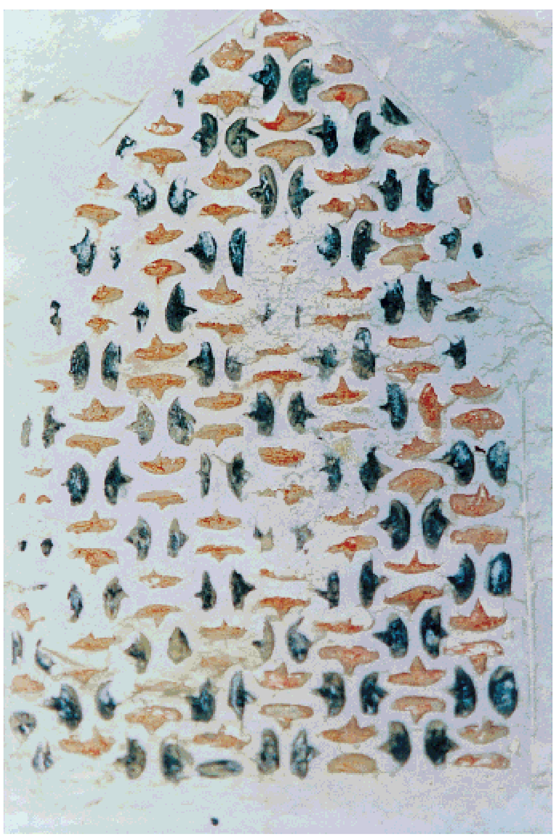

Figure 2. Specimen of the polychrome fresco decorations in the Convento de la Peregrina; the Islamic influence is recognizable.

artwork had been isolated for some 500 years since closure of the Convent following outbreaks of pestilence in the 14th Century. The paintings and decorations are significant in that they clearly show Islamic influence (Fig. 2) in a Christian church situated on a most important pilgrim route, that of the Camino de Santiago, extending from Southern France to Santiago de Compostela in Galicia. The frescoes are showing signs of serious damage and our pigment studies were undertaken as part of a restoration project. During these studies, the significance of the presence of large areas of lichen invasion of the outer walls of the Convento de la Peregrina became apparent; preliminary studies suggested that several regions of the frescoes had suffered a staining and damage which indicated a possible lichen source, given the conditions and climatic dampness which had been generated by the closure of the chapel.

EXPERIMENTAL

Samples

Lichen encrustations with substrata were taken from the outer wall of the Convento de la Peregrina, Sahagún, Spain. The sampling area was

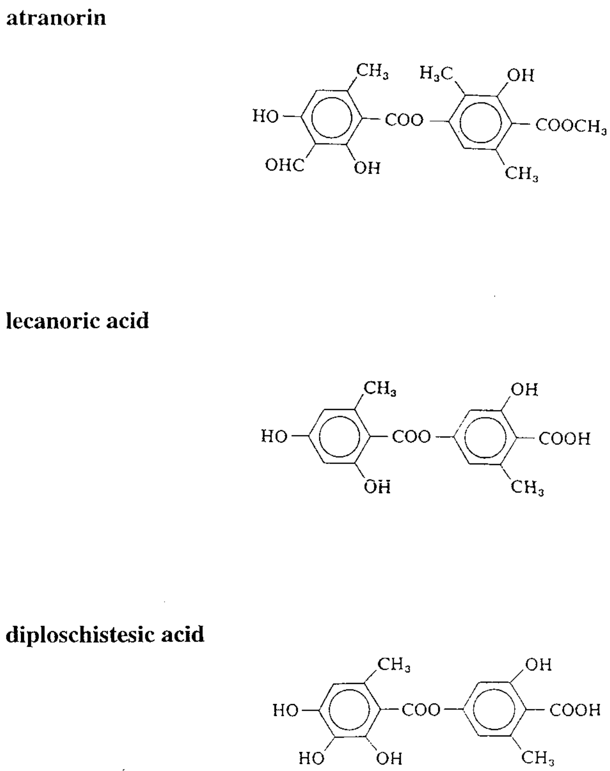

Figure 3. Three important phenolic lichen acids produced by *Diploschistes scruposus.*

the pillar situated to the left of the entrance door (Fig. 1); extensive colonization of the lower walls, pillars, and window surrounds of the Convent has occurred. We believe that lichen invasion of the chapel itself took place through the unglazed windows and has contributed to the biodeterioration of the polychrome frescoes inside the chapel.

The lichen, *Diploschistes scruposus,* is an aggressive colonizer of calciferous substrata and, in addition to oxalic acid, produces atranorin, lecanoric acid, and diploschistesic acid in its encrustations.[15] These are polyphenolic lichen acids of the *para*-depside type (Fig. 3), which differ in the substitution patterns and methylation of the phenolic rings. The most characteristic functional chemical features between the three lichen acids are provided by atranorin, which contains the aldehyde and methyl ester groupings.

Raman Spectroscopy

Fourier transform Raman spectra were obtained from several samples of lichen-substratal encrustations using a Bruker IFS 66 instrument with FRA 106 Raman module attachment. The grayish-white lichen thallii were intimately associated with a white encrustation which contained the lichen metabolic products and the products of their reaction with the yellow calcareous substratum. The substratal damage was extensive and the underlying rock crumbled very easily; evidence for the destructive power of this particular lichen species for monumental stonework could not be more conclusive.

Spectra were recorded with 1064 nm excitation using 8 cm^{-1} spectral resolution and between 1000 and 8000 scans accumulated. Typically, a laser power of 40 mW was used to minimize sample decomposition; the diameter of the spot at the sample was 100 μm. Band wavenumber positions are accurate to ± 1 cm^{-1}. The Raman spectra were corrected for white-light response.

Several sampling positions were undertaken for each lichen-substratal specimen, involving the upper surface, the lichen encrustation, and the substrate.

RESULTS AND DISCUSSION

A typical spectrum of the upper surface of a lichen-substratal encrustation is shown in Figure 4 for the 2600–3400 cm^{-1} region and Figure 5 for the 50–1800 cm^{-1} region. The Raman spectra clearly indicate several features which arise from organic compounds:

1. In the higher wavenumber region, the weak bands at 3049 cm^{-1} and 3065 cm^{-1} are characteristic of aromatic and ν(C=CH) aliphatic stretching vibrations.[5,6] The strongest intensity in this wavenumber region is represented by the $\nu(CH_3)$ and $\nu(CH_2)$ modes at 2937 and 2903 cm^{-1} with weaker bands due to aliphatic ν(CH) modes at 2985 and 2853 cm^{-1}.[16,17]
2. The most noteworthy features in the Raman spectrum of the 200–1750 cm^{-1} region are the strong bands at 1524, 1156 cm^{-1} which are characteristic of the ν(C=C) and ν(C—C) modes of β-carotene,[7,18] a pigment frequently found in lichen thalli. The doublet at 1488, 1463 cm^{-1} is characteristic of calcium oxalate monohydrate (whewellite), $CaC_2O_4 \cdot H_2O$, which is formed from the reaction of oxalic acid produced by the lichen hyphal mycobiont and calcareous substrata.[13] Other modes due to oxalate ion in whewellite are the ν(C—C) band at 895 cm^{-1} and $\delta(CO_2)$ at 503 cm^{-1}.[13]

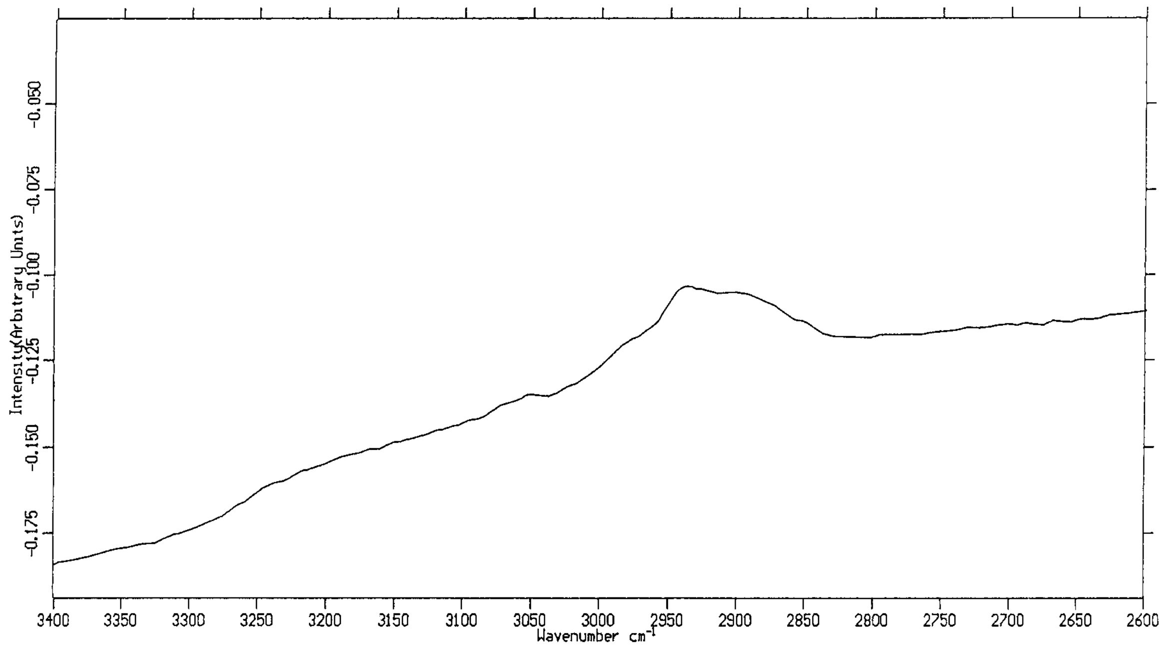

Figure 4. FT Raman spectrum of the lichen encrustation of *Diploschistes scruposus;* samples removed from colonies on outer walls of the Convento de la Peregrina. 1064 nm excitation, 8 cm^{-1} spectral resolution, 4000 scans accumulated, wavenumber range 2600–3400 cm^{-1}.

The medium-strong band at 1325 cm^{-1} is attributed to chlorophyll in the thalli. Weaker bands at 1654 and 1630 cm^{-1} are ascribed to quinonoid features, probably from a lichen anthraquinone pigment such as parietin.[19] The weak band at 1725 cm^{-1} is attributed to the

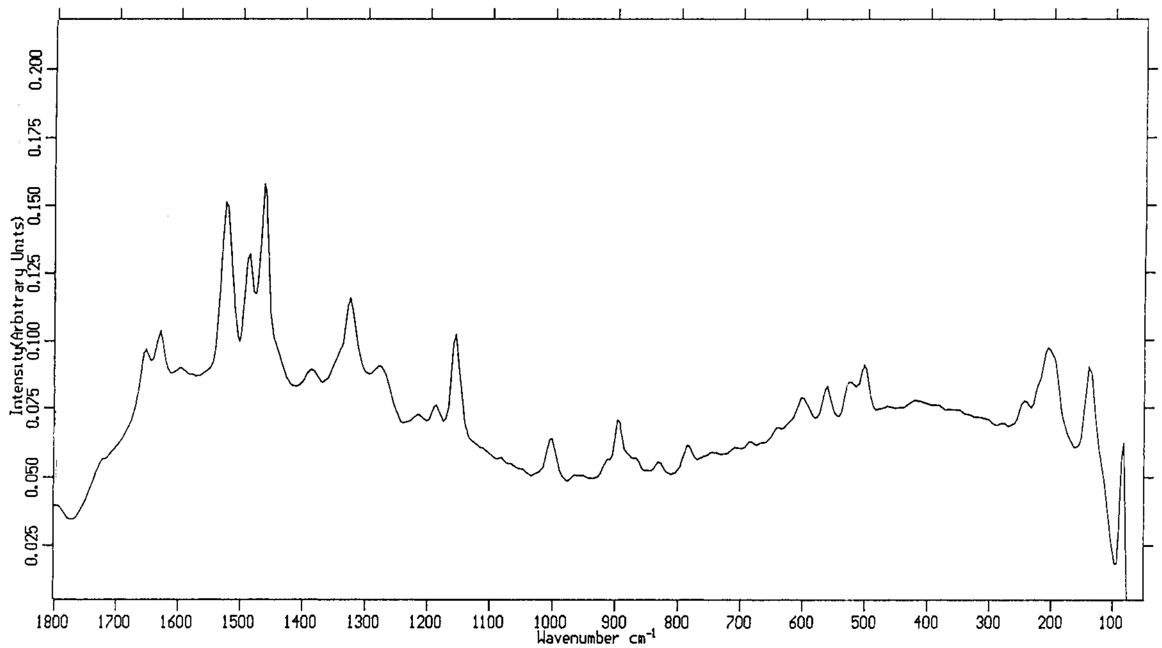

Figure 5. FT Raman spectrum of the lichen encrustation of *Diploschistes scruposus;* conditions as for Figure 4 but wavenumber range 50–1800 cm^{-1}.

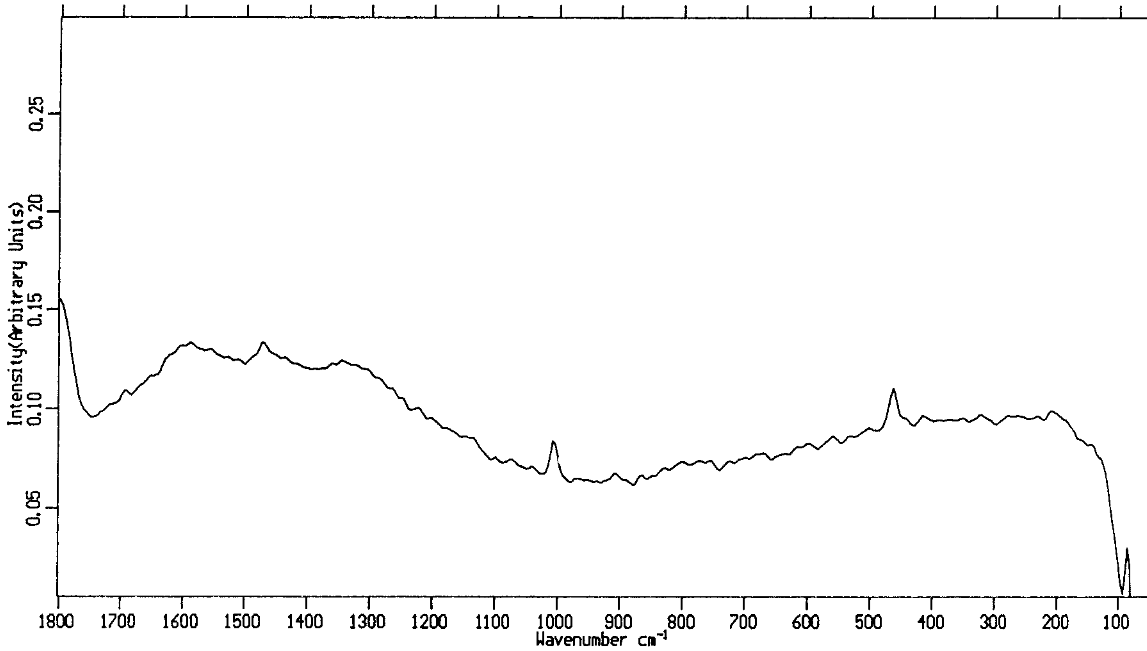

Figure 6. FT Raman spectrum of specimen of black pigment from frescoes in Convento de la Peregrina; conditions as for Figure 5.

ν(C═O) of the aldehyde moiety and ester in atranorin,[16] whereas the band at 1003 cm^{-1} is the ν(CC) ring symmetric stretch of a substituted aromatic ring; the weaker band at 1549 cm^{-1} is the quadrant ring ν(CCH) stretching mode of an aromatic compound, such as that provided by the para-depsides here.[16] Other weak modes in the vicinity of 1370, 1220 cm^{-1} are $\delta(CH_2)$ deformation and scissors (wagging) modes. Those near 600 and 560 cm^{-1} are characteristic of the —COO— ring linkage deformation modes of the phenolic acids.[16,17]

Of equal interest in the case of this lichen-substratal spectral analysis is the absence of bands characteristic of the substratum. Whereas our previous studies of aggressive colonizers such as *Dirina* or *Lecanora* have shown evidence[6,7] in the Raman spectra for the incorporation of material such as calcite (1086 cm^{-1}), gypsum (1008 cm^{-1}), and quartz (463 cm^{-1}), there is no indication here that substratal incorporation has taken place. Despite this, the friable nature of the underlying substratum bears witness to the deleterious effects of the hyphal penetration and lichen acid secretion for this particular colonization.

In a recent study,[7] we have noted the effect of geographical location and climate on the ability of *Dirina massiliensis* forma *sorediata* to both biodeteriorate and incorporate substratal material into its encrustations. The Renaissance frescoes at the Palazzo Farnese in Caprarola[12] painted on gypsum-coated marble have suffered greatly from invasion of this lichen species since 1986. In one square meter of coverage over one kilo of calcite substratum has been eroded by the lichen colonization and converted into calcium oxalate monohydrate.[6]

In the Convento de la Peregrina at Sahagún, it is clear that extensive lichen invasion of the outer walls has already occurred; the extent of the white covering can be seen in Figure 1. However, the result of the invasion inside the chapel is even more serious since the important late medieval frescoes painted in an Islamic style appear to be endangered from biodeterioration. The latter process appears to adopt two forms, namely

1. a leaching-out of red ocher from nearby pigmentation and substrate iron(III) oxide by lichen acids; the *para*-depsides shown in Figure 3 are good complexing agents of transition metal ions such as Fe(III). The curious patterns of stains ("mancha") on otherwise unmarked fresco is possibly indicative of previous lichen hyphal activity.
2. On some samples of black paint fragment excised from the frescoes a rather curious Raman spectrum is given (Fig. 6). This can be explained by the residual trace of lichen activity evidenced by the band at 1474

cm^{-1}, sandwiched between the broader features at 1590 and 1340 cm^{-1} characteristic of lampblack or soot. The band at 1008 cm^{-1} is substratal gypsum, and that at 465 cm^{-1} is α-quartz.[19,20] Other very weak features at 909 and 510 cm^{-1} are oxalate ion modes, ν(C—C) and $\delta(CO_2)$, respectively.[13] The observation of just a singlet at 1474 cm^{-1} instead of a doublet at 1488 and 1463 cm^{-1} is itself of interest since calcium oxalate dihydrate (weddellite) has a single ν(C═O) stretching mode at 1474 cm^{-1}.[13] The chapel had been closed for some 500 years until its reopening in 1956; a damp atmosphere within is conducive to the hydration change of the calcium oxalate from monohydrate to dihydrate, which is also favored by lower temperatures, as our work with Antarctic epilithic and cryptoendolithic lichen species has shown.[9,19,20]

CONCLUSIONS

The results of our study of the lichen colonization of the Convento de la Peregrina in Sahagún, Spain, indicate the rich chemistry of the biodeterioration process which is undoubtedly occurring there on the outer walls. Of great concern, however, is the spectroscopic evidence for possible lichen damage to the interior walls, especially those containing medieval frescoes. Monitoring of the interior climatic conditions of this important monument is clearly required.

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