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Analytical Pyrolysis of Lichen Thalli

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Abstract

Samples of *Lecanora muralis* collected from polluted and non-polluted areas were studied by means of pyrolysis-gas chromatography and pyrolysis-gas chromatography-mass spectrometry. The major difference between them was the presence of an unresolved complex mixture of compounds in the chromatogram of the sample removed from limestone of the cathedral of Sevilla. This mixture has been found to be characteristic of petroleum contamination. In addition, dehydration products from hopanediols and hopanetriols were found. It appears probable that airborne particles and aerosols present in polluted environments are entrapped in or deposited onto the lichen thallus, thus yielding the evolved petrogenic compounds.

Keywords: pyrolysis gas chromatography, pyrolysis gas chromatography-mass spectrometry, petroleum hydrocarbons, hopanoids, steranes, lichens, *Lecanora muralis*, atmospheric pollution, stone biodeterioration

1. Introduction

Atmospheric pollution is generally recognized as a significant factor in the deterioration of cultural properties (Camuffo et al., 1982, 1983; Cheng et al.,

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1987) but stonework biodeterioration deserves more attention than it has received. Diverse bacterial (Bock, 1987; Krumbein, 1972) and fungal (Krumbein, 1972; 1973) species promote stone weathering. In this respect, fungal growth has been observed to be enhanced by the presence of organic volatile molecules in the atmosphere (Rasmussen et al., 1968). Likewise, the environmental conditions prevailing in big cities, associated to all sorts of pollution but specially airborne petroleum residues (Rosell et al., 1991), stimulate the development of heterotrophic microflora (Krumbein, 1973; Krumbein and Schönborn-Krumbein, 1987).

Some authors have stressed the role of lichens in the formation of calcium oxalate patinas (whewellite and weddellite) on marbles and limestones of monuments and statues (del Monte et al., 1987). Seaward (1988) suggested that changes in environmental pollution levels may conduce to increasing detrimental invasion by certain lichen species.

In general, the lichen flora of urban areas is poor. However, *Lecanora muralis* is recognized by its high tolerance to polluted urban environments so that it readily adapts to man-made substrates and spreads towards the urban center. In this respect, we have found distinctive distributions of *L. muralis* on all the Spanish cathedrals that we have investigated. The presence of lichen mosaics is a characteristic feature of southern European cathedrals with respect to those from northern Europe. Several species appear as a dark rust-brown cover that upon ageing resemble black sulfated crusts (Saiz-Jimenez and Garcia del Cura, 1991.). Most lichen species are innocuous and may also afford protection to the stone against pollutant gases. An exception is *Lecania erysibe*, causing damage by pulling away and scaling important limestone fragments in Sevilla's cathedral belfry (Saiz-Jimenez, 1981).

Further insight into the influence of urban pollution on lichen growth and stone weathering can be obtained from the differentiation of biogenic and anthropogenic inputs in the degraded surfaces which can be achieved through the study of the organic compounds attached to the building walls. In a search for a fast analytical method that did not require elaborated sample handling procedures, pyrolysis was applied to both sulfated crusts (Saiz-Jimenez, 1991) and lichen thalli. *Xanthoria parietina, Candelariella vitellina, Lecania erysibe* and several *Lecanora muralis* samples were pyrolysed. In this communication we report the data obtained when *L. muralis* from rural and urban areas were studied by means of pyrolysis-gas chromatography and pyrolysis-gas chromatography-mass spectrometry.

2. Materials and Methods

The crustose lichen *Lecanora muralis* was chosen because it is very common and abundant in rural and urban environments. The samples were obtained from the following sites:

- *Lecanora muralis* (Schreb.) Rabenh. Finca El Galeon, Cazalla de la Sierra, Province of Sevilla, on micaschist, 40 m a.s., UTM TG5497, collected 14 October 1983.
- *Lecanora muralis* (Schreb.) Rabenh. var. *dubyi* (Müll. Arg.) Poelt. Loma la Braña, Sierra del Aljibe, Province of Cadiz, on sandstone, 1000 m a.s., UTM TF6644, collected 2 December 1983.
- *Lecanora muralis* (Schreb.) Rabenh. From limestone of the cathedral of Sevilla, 10 m a.s., collected 17 May 1988.

Curie-point pyrolysis-gas chromatography

Small pieces (20–200 μg) of lichen thallus were applied to ferromagnetic wires by pressing the dry samples on the wire. The wires were heated within 0.1 s to their Curie temperature (in this case 770°C) and were kept at this temperature for 10 s. The pyrolysis was carried out using a pyrolysis reactor which was directly mounted on the injection block of a Varian 3700 gas chromatograph. The temperature of the injection block was 250°C. Separation of the pyrolysis products was performed on a fused silica capillary column (25 m $\times$ 0.32 mm) coated with DB 1701, using helium as carrier gas. The temperature was programmed from 30 to 290°C (5 min) at a rate of 3°C/min. The gas chromatograph was equipped with a flame ionization detector.

Curie-point pyrolysis-gas chromatography-mass spectrometry

The analysis was performed on a Hewlett-Packard 5840 gas chromatograph connected with a VG-70S mass spectrometer operated at 70 eV and a cycle time of 1.8 s. The gas chromatography was equipped with a fused silica capillary column (25 m $\times$ 0.32 mm) coated with CP sil-5 (film thickness 0.12 μm) and was operated with helium as carrier gas. The temperature was programmed from 0°C, by using a cryogenic unit, to 300°C (20 min) at a rate of 3°C/min. Mass range m/z 20–450 up to scan 250 and m/z 50–800 after scan 250; m/z 28, 32, 40 and 44 were omitted from the reconstructed total ion currents. The instrumental pyrolysis analyses were performed in the Organic Geochemistry Unit, Delft University of Technology.

3. Results and Discussion

Pyrolysis is an useful method for the chemical characterization of complex biological materials (Saiz-Jimenez, 1988). Upon pyrolysis, materials such as those present in microbial and plant cell walls undergo thermally induced bond cleavages. The process results in the partial fragmentation of the complex macromolecules and produces volatile products that can be analysed by gas chromatographic techniques. This method affords the easy recognition of polysaccharides, proteins, nucleic acids, etc. from the analysis of the pyrolysis products. Low-molecular-weight molecules are evaporated under pyrolysis conditions.

The separation of the mixture of evaporated/pyrolyzed species by gas chromatography provides structural information and gives rise to a pyrogram pattern that may afford a distinctive fingerprint of the material. Pyrograms have proven to be a useful source of information and classification of organisms (O'Donnell et al., 1980).

However, pyrolysis-gas chromatography of bacteria and fungi is seriously hampered by effects related to growth media and growth time. Oxborrow et al. (1977a,b) observed that samples of *Bacillus* spp. grown on different media and incubation times exhibited different pyrograms which prevented the identification and comparison of the species under study.

In this respect lichen manipulation is easier because no isolation or culturing are needed. Small pieces of thallus (20–200 μg) can be analysed directly and the pyrogram is representative of the organic matter constituting the organism.

Previous unpublished works have demonstrated that polysaccharide-, protein-, chlorophyll- and tocopherol-derived pyrolysis products as well as fatty acids and aliphatic hydrocarbons constitute the bulk of organic compounds produced upon lichen pyrolysis. An example of this type of product mixture is shown in Fig. 1 (a and b) where the pyrograms corresponding to *L. muralis* var. *dubyi* and *L. muralis* are displayed.

Interestingly, both pyrograms exhibit a rather similar pattern. However, the pyrograms from *L. muralis* have been observed to be different from those obtained from *X. parietina* and *C. vitellina*, suggesting that this technique may perhaps be used for the differentiation between genera and species and for the chemical assessment of the classification of species in varieties.

In any case, the similarity of the profiles of these two lichen varieties is particularly interesting for the purposes of the present study because the two samples were collected in very clean environments. These pyrograms can therefore be interpreted as a baseline level of biogenic compounds in cases of no pollution.

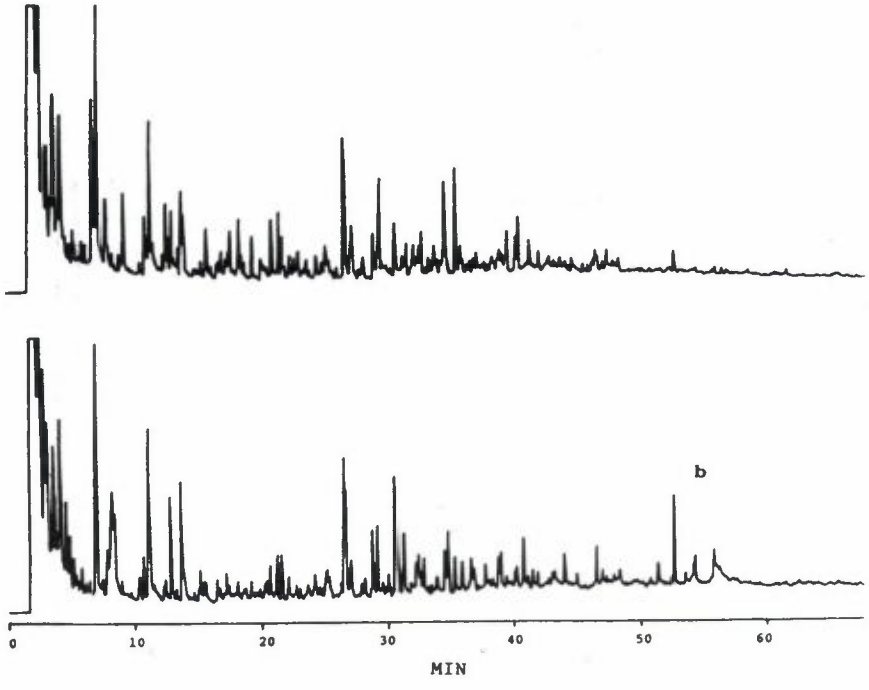

Figure 1. Curie-point gas chromatography traces of (a) *Lecanora muralis* var. *dubyi* (Aljibe) and (b) *Lecanora muralis* (Cazalla).

The lack of petrogenic pollution in these samples is also reflected in the absence of petroleum indicators such as an unresolved complex mixture (UCM) of compounds. Petroleum contamination is usually recognized by the occurrence of an UCM and distinct distributions of hopanes and steranes (Albaiges and Albrecht, 1979) that will be discussed later. On the contrary, such UCM has been observed in pyrolysis mixtures of black sulfated crusts removed from historic buildings and monuments located in polluted urban areas (Saiz-Jimenez, 1991 Saiz-Jimenez and Garcia del Cura, 1991).

More information than retention time data is required for the identification of the compounds eluting on the pyrograms. For this purpose GC-MS systems with computerized data acquisition are used.

Accordingly, Fig. 2 shows the reconstructed pyrolysis-GC-MS total ion current trace of a *L. muralis* collected on the limestone of the cathedral of Sevilla. The pyrolysis products have been identified by comparison of their mass spectra with library spectra data as well as with the mass spectra and

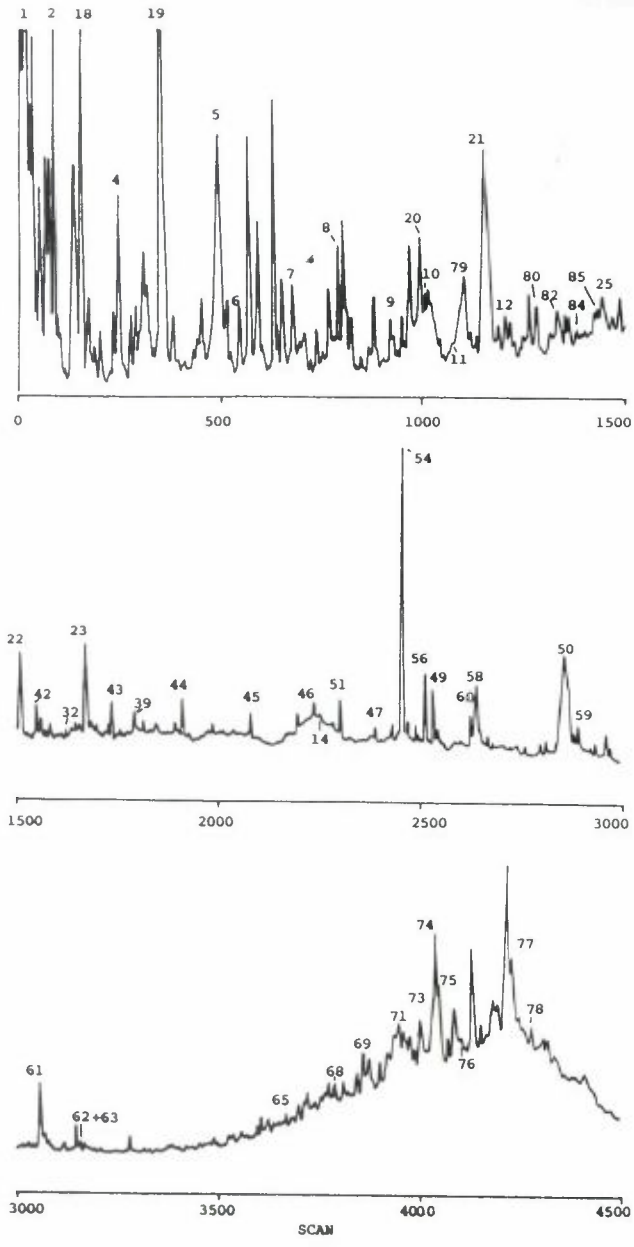

Figure 2. Total ion current trace of the Curie-point gas chromatography-mass spectrometry run of *Lecanora muralis* collected in the cathedral of Sevilla. Peak identifications are given in Tables 1–4 and text.

retention time of standard compounds. Pyrolysis-GC-MS runs of reference materials such as polysaccharides, proteins, cyanobacteria and bio- and geopolymers have also been performed (van de Meent et al., 1980; Saiz-Jimenez and de Leeuw, 1984; Nip et al., 1986; Gadel and Bruchet, 1987; Chalansonnet et al., 1988; Hatcher et al., 1988).

Owing to the vast number of identified compounds the individual molecules are presented and discussed in groups according to their parent materials, as most of the major compounds are known pyrolysis products of biologically produced substances (polysaccharides, proteins, lipids, etc.) (Saiz-Jimenez, 1988; Saiz-Jimenez and de Leeuw, 1984; van der Kaaden et al., 1983).

The compounds listed in Table 1 are the pyrolysis products characteristic of polysaccharides. They have been identified in pyrolysates of cellulose, amylose, soil polysaccharides and cyanobacteria (van der Kaaden et al., 1983; Boon,1984; Saiz-Jimenez, 1988; Saiz-Jimenez et al., 1990). The abundance of levoglucosan that is a specific marker of glucose, the presence of pyranones, and the more general carbohydrate indicators of the furan series indicate that a glucose polymer determines the polysaccharide composition. This is consistent with the fact that cellulose and glucans have been found to constitute an

Table 1. Pyrolysis products from polysaccharides

Peak	Compound
1	Furan
2	2-Methylfuran
3	3-Methylfuran
4	2,5-Dimethylfuran
5	Furaldehyde
6	Furfuryl alcohol
7	C_3-Alkylfuran
8	5-Methyl-2-furaldehyde
9	4-Hydroxy-5,6-dihydro-2H-pyran-2-one
10	4-Hydroxy-6-methyl-5,6-dihydro-2H-pyran-2-one
11	3-Hydroxy-6-methyl-3,4-dihydro-2H-pyran-2-one
12	3-Hydroxy-2-methyl-4H-pyran-4-one
13	5-Hydroxy-2-methyl-4H-pyran-4-one
14	Levoglucosan

important part of the lichen thallus, and starch is considered as the storage product of the phycobiont (Hale, 1983).

Chitin pyrolysis products were only detected as minor constituents of the lichen pyrolysates. Therefore, no special attention has been devoted to the identification of these compounds despite that the hyphal cell walls of lichens are composed of chitin fibrils embedded in an amorphous glucan matrix (Hale, 1983).

The pyrolysis of polyamino acids, proteins and complex proteinaceous materials was recently studied by Boon and de Leeuw, 1987; Saiz-Jimenez,1988; and Saiz-Jimenez et al., 1990. Table 2 lists some of the specific pyrolysis products with indication of the amino acid from which they derive. A more detailed description of the 18 derivatives providing sequence information on pairs of aliphatic amino acid moieties (VAL, LEU, ILEU) can be found elsewhere (Boon and de Leeuw, 1987). All these pyrrole-2,4-diones and pyrrolidine-2,4-diones were identified in cyanobacteria (Saiz-Jimenez et al., 1990) and in this work. These pyrolysis products are usually identified by selective mass chromatography on m/z 152, 166, 180, 181, 195 and 209.

It should be noted that although some aromatic compounds (e.g. benzene, toluene, phenol and cresol) have been attributed to pyrolysis of phenylalanine and tyrosine, in the pyrolysis of lichen thallus it is likely that the major contributors to these and other phenolic compounds are orcinol depsides synthesized by the lichen. In this respect it has been demonstrated that thermal

Table 2. Pyrolysis products from proteins

Peak	Compound	
15	2-Methylpropanal	(valine)
16	3-Methylbutanal	(leucine)
17	2-Methylbutanal	(isoleucine)
18	Benzene	(phenylalanine)
19	Toluene	(phenylalanine)
20	Phenol	(tyrosine)
21	Cresol	(tyrosine)
22	Indole	(tryptophan)
23	Methylindole	(tryptophan)
24–32	3,5-alkyl-3,4-dihydro-2H-pyrrole-2,4-diones	
33–41	3-alkenyl-5-alkyl-pyrrolidine-2,4-diones	

decomposition of lichen depsides leads to decarboxylated compounds and phenolic units (Huneck et al., 1989). Thus, in the pyrolysate of lichen thallus, in addition to the abundant phenol (29) and *m*-/*p*-cresol (21), *o*-cresol (79) and several C_2-alkyl- and C_3-alkylphenols (80–85) have been identified.

Lipid molecules are also present (see Table 3). Their origin may be either from evaporation or pyrolytic reactions. The series of aliphatic hydrocarbons (n-alkanes and n-alkenes) is common to cyanobacteria, algae and fungi and most probably correspond to evaporation products, although an origin related with n-alkanoid acid decarboxylation cannot be discarded. The distribution of fatty acids is dominated by the C_{16} and C_{18} homologs. They are presumably related to free moieties or bound to cell wall components. These are the most predominant fatty acids found in biological samples (Saiz-Jimenez et al., 1990).

The phytol esters of chlorophylls appear as phytadienes and phytenes in the pyrolysates. The phytadiene isomers have a characteristic distribution which is also observed in cyanobacteria and higher plant-derived materials (Saiz-Jimenez et al., 1990). The pyrolysis of tocopherols also yield pristenes (Goosens et al., 1984). Longer chain isoprenoid hydrocarbons such as C_{35} aliphatic homolog have also been identified.

The hopanoids constitute a major group of lipids in this lichen sample (Table 4). They are predominated by a hopanone that occurs along with diverse hopadienes and hopatrienes. These unsaturated species are likely dehydration products of the characteristic hopanediol and hopanetriol constituents of lichens, i.e. hopane-6α,22-diol (zeorin), hopane-7β,22-diol, hopane-15α,22-diol (Ronaldson and Wilkins, 1978; Elix et al., 1982; Wilkins et al., 1989).

Table 3. Lipid moieties in the scan range 1 to 3100

Peak	Compound
	Alkanes
42–50	Alkenes
51	Prist-1-ene
52	Phytene
53–57	Phytadienes
58–59	Fatty acids
60	Cyclopentyloctadecane
61	Cyclohexyltetradecane
	Polycyclic aromatic hydrocarbons

Table 4. Lipids identified in the scan range 3100 to 4500

Peak	Compound
62	*n*-Docosane
63	13-Methylpodocarpa-8,11,13-triene
64	24-Ethyl-5α(H),14α(H),17α(H)-cholestane 20S
65	24-Ethyl-5α(H),14α(H),17α(H)-cholestane 20R
66	24-Ethylsteratriene
67	17α(H),21β(H)-norhopane
68	Hopadiene
69	17α(H),21β(H)-hopane
70	17α(H),21β(H)-homohopane
71	Hopatriene
72	Hopadiene
73	17α(H),21β(H)-bishomohopane
74	Hopanone
75	C_{35} isoprenoid hydrocarbon
76	17α(H),21β(H)-trishomohopane 22S
77	17α(H),21β(H)-trishomohopane 22R
78	17α(H),21β(H)-pentaquishomohopane

In addition to these oxygenated compounds a series of $C_{29} - C_{35}$ 17α(H), 21β(H)hopanes is present. They originate from the transformation of the biosynthesized 17β(H), 21β(H) configuration to the 17α (H) epimers upon geochemical reactions (Ensminger, 1977; Mackenzie et al., 1980). They are commonly found in petroleum products and their occurrence in recent environments and atmospheric particles is generally attributed to petroleum pollution (Simoneit, 1984a).

Petroleum inputs are also represented by other lipid molecules such as mixtures of cholestanes, alkylcyclohexanes and alkylcyclopentanes (Simoneit, 1985). These compounds are produced by the thermocatalytic reactions associated with petroleum formation and, similarly to the 17α (H), 21β(H)-hopanes, their occurrence in atmospheric particles is related to petroleum products (Simoneit et al., 1988).

Garty and Delarea (1987) observed that in the course of thallus formation, dust particles become incorporated in the lichen structure. However, in urban

environments, oil-fired and coal-fired particles are abundant. It appears that airborne carbonaceous particles become entrapped in the developing thallus or deposited onto the surface of *L. muralis*. These carbonaceous particles are a source of organic components derived primarily from fossil fuel utilization by vehicles and power plants (Simoneit, 1984b).

In conclusion, the application of analytical pyrolysis to lichens allows the overall chemical characterization of the organic matter present in lichen thallus. This method could also be used for taxonomic purposes or for identification of metabolites. In this connection, evaporation and/or pyrolysis at low temperatures (358–510° C) could provide useful data on lichenic compounds on a microscale level, as the advantage of pyrolysis is the very minute amount of sample required.

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