CHEMICAL COMPOSITION OF THE LICHEN PHYSCIA MEDITERRANEA NIMIS: A BRIEF REVIEW

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Abstract. *Physcia mediterranea Nimis is a rare saxicolous lichen of the Mediterranean–Atlantic region whose chemistry has remained largely unexplored. This short review summarizes its taxonomy and the single comprehensive phytochemical study available (Kerboua et al., 2021), in which an Algerian specimen was extracted with n-hexane and methanol and analysed by GC–MS, HPLC–ESI-MS/MS, and NMR. More than one hundred constituents were detected, including depsides (atranorin, chloroatranorin), benzoic acid derivatives (atraric acid, sparassol), saturated and unsaturated fatty acids, paraconic acids, phenolics, sesquiterpene lactones, triterpenes, and—reported for the first time in a lichen—a kaurane diterpene, (−)-ent-kauran-16α-ol. Atranorin was confirmed by NMR as the dominant cortical metabolite. The species is a promising source of bioactive compounds, yet direct bioassays, quantitative profiling, and studies of ecological variability are still lacking.*

Keywords: *Physcia mediterranea; lichen secondary metabolites; atranorin; atraric acid; depsides; GC–MS; HPLC–ESI-MS/MS; NMR*

1. Introduction

Lichens are symbiotic organisms formed by a fungus (mycobiont) and a photosynthetic partner (photobiont). More than seventeen thousand species are known worldwide, and they are notable for synthesizing over eight hundred unique secondary metabolites—including depsides, depsidones, dibenzofurans, xanthones, usnic acid, and terpenoids—with antioxidant, antimicrobial, anti-inflammatory, antiviral, and antitumour activities of pharmaceutical and cosmetic interest.

Members of the genus Physcia (Physciaceae) typically accumulate atranorin and terpenoids in the cortex, where these compounds act as ultraviolet screens. Physcia mediterranea Nimis is a rare saxicolous species of the Mediterranean–Atlantic region that, although described taxonomically since 1970, remained chemically almost

unstudied until recently. The aim of this review is to compile and critically evaluate the available taxonomic, ecological, and phytochemical data for the species and to identify the principal gaps in current knowledge.

2. Materials and Methods

This work is a literature-based review. Sources were retrieved from PubMed, Google Scholar, MDPI, and ResearchGate, and from the taxonomic resources ITALIC, Index Fungorum, and GBIF. The only comprehensive primary source on the chemistry of the species is the study by Kerboua et al. (2021).

In that study, a saxicolous specimen collected in June 2017 from the El-Kala National Park, Algeria (36°49′09″ N, 08°31′33″ E; 120 m a.s.l.), was extracted with n-hexane in a Soxhlet apparatus (24 h). The extract was partitioned with hot methanol (60 °C) into a methanol-insoluble wax fraction and a methanol-soluble fraction. The fractions were analysed by GC–MS (Agilent 7890A; methanol-soluble fraction methylated with diazomethane; EI, 50–600 a.m.u.), HPLC–ESI-MS/MS (Thermo Q-Exactive Orbitrap, Kinetex XB-C18 column; negative mode, 100–1000 a.m.u.), and $^{1}H/^{13}C$ NMR (Bruker Avance III, 400/100 MHz, $CDCl_3$).

3. Results and Discussion

Taxonomy and distribution. P. mediterranea (Fungi, Ascomycota, Lecanoromycetes, Physciaceae) derives from the basionym Physcia aipolia subsp. scopulorum Lambinon & Vězda (1970) and was raised to species rank by Nimis (2016). The thallus is foliose, narrow-lobed, forming rosettes 3–8(–10) cm wide; ascospores are one-septate, brown, 14–19 × 6–8(–10) µm. It is a Mediterranean–Atlantic silicicolous species of coastal rocks, known from Italy, Iberia, the Canary Islands, and Greece, and reported in 2021 for the first time from Algeria, which extended its known range (Table 1).

Table 1.

Principal taxonomic and ecological parameters of P. mediterranea.

Parameter	**Information**
Family / Genus	Physciaceae / Physcia
Basionym	Physcia aipolia subsp. scopulorum Lambinon & Vězda (1970)
Thallus	Foliose, narrow-lobed, 3–8(–10) cm rosettes
Ascospores	One-septate, brown, 14–19 × 6–8(–10) µm
Substrate	Coastal siliceous rocks (saxicolous)
Distribution	Mediterranean–Atlantic; Italy, Iberia, Canary Islands, Greece, Algeria

Chemical composition. The two fractions were analysed separately. In the wax fraction, HPLC–ESI-MS/MS detected 45 peaks (37 identified), and NMR confirmed atranorin as the dominant metabolite. In the methanol-soluble fraction, GC–MS resolved 10 components (9 identified) and HPLC–ESI-MS/MS 54 compounds (50 identified). Sixteen compounds were common to both fractions. The constituents span paraconic and aliphatic acids, aromatic polyketides (depsides, depsones, phenyl ethers), phenolic acids, sesquiterpene lactones, and triterpenes.

GC–MS of the methanol-soluble fraction. Methylated benzoic acid derivatives (atraric acid, sparassol) accounted for ≈ 56 % and free fatty acids for ≈ 36.1 %, with palmitic acid alone ≈ 24 % (Table 2). The most significant finding was the kaurane diterpene (−)-ent-kauran-16α-ol (≈ 3.8 %), never previously reported in a lichen. Atraric acid is an androgen-receptor antagonist with anti-prostate-cancer, antioxidant, and antimicrobial activity.

Table 2.

Major compound groups identified by GC–MS (methanol-soluble fraction).

Compound group / component	**Proportion (%)**	**Remarks**
Benzoic acid derivatives (atraric acid, sparassol)	≈ 56	Depside / depsidone precursors
Free fatty acids (total)	≈ 36.1	Palmitic 24; oleic 4.2; stearic 3.8; linoleic 3.2
(−)-ent-Kauran-16α-ol	3.8	First report in a lichen
Unidentified	≈ 2.2	—

HPLC–ESI-MS/MS and NMR. The wax fraction was rich in paraconic and aliphatic acids (e.g. fumaric, traumatic), phenolics (p-coumaric acid, esculetin), and the depsides atranorin ($[M-H]^-$ m/z 373.0929) and chloroatranorin ($[M-H]^-$ m/z 407.0539). The methanol-soluble fraction additionally yielded depsides, a depsone (allo-protolichesterinic acid), a sesquiterpene lactone (bakkenolide A), a diphenyl ether (leprolomin), and the triterpenes muronic and ursolic acid (Table 3). Esculetin and p-coumaric acid were detected in lichen material for the first time. NMR confirmed atranorin as the dominant cortical metabolite, consistent with the chemotaxonomy of the genus and its photoprotective role against UV radiation.

Table 3.

Selected bioactive compounds identified in P. mediterranea.

Compound	Chemical class	Notable feature
Atranorin	Depside (β-orcinol)	Dominant metabolite; UV protection, antioxidant, antimicrobial
Atraric acid	Methylated benzoic acid	Androgen-receptor antagonist; anti-prostate-cancer
(−)-ent-Kauran-16α-ol	Diterpene (kaurane)	First report in a lichen
Esculetin	Coumarin	First report in a lichen; antiviral, antitumour
Ursolic acid	Triterpene	Antitumour
Asebotoxin I	Toxic diterpene	Previously known only from Pieris japonica

State of knowledge and gaps. The chemistry of P. mediterranea is exceptionally little studied: only one comprehensive analysis exists, based on a single Algerian population. Although atranorin confirms the genus signature, compounds such as the kaurane diterpene, esculetin, and asebotoxin I are unexpected and may serve as new chemotaxonomic markers. The main limitations are that biological activity was not measured directly in the species' extracts, only one solvent system was used, geographic and seasonal variability was not examined, and most constituents were identified only qualitatively. The rarity of the species also raises conservation concerns.

4. Conclusions

P. mediterranea is taxonomically well described but, until the 2021 study, chemically almost unstudied.

GC–MS, HPLC–ESI-MS/MS, and NMR revealed more than one hundred constituents, dominated by atranorin, chloroatranorin, atraric acid, fatty acids, paraconic acids, phenolics, and triterpenes.

A kaurane diterpene, (−)-ent-kauran-16α-ol, was reported for the first time in a lichen, alongside esculetin and asebotoxin I.

The species is a promising source of bioactive compounds for pharmaceutical and cosmetic applications.

Direct bioassays, multi-solvent extraction, quantitative profiling, comparison of populations, and conservation-aware sampling are needed in future work.

Conflict of Interest

The authors declare no conflict of interest.

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