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SHORT COMMUNICATION

SOME OCCURRENCES OF THE ANTHRAQUINONE PARIETIN IN LICHENS*

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Abstract—The presence of parietin in *Pyrenula cerina, Arthonia elegans, Biatorella conspersa, B. ochrophora, Sphaerophorus fragilis, Trypethelium aeneum,* and *T. aureomaculata* is reported, and the question of its occurrence in *Stereocaulon corticatulum* v. *procerum* is discussed. The finding of parietin in lichens outside the Teloschistaceae does not diminish its taxonomic significance within this family.

INTRODUCTION

IN LICHENS, parietin (I) has long been supposed to occur only in species belonging to the family Teloschistaceae.† In 1965 Huneck and Follmann[1] isolated parietin from the Stereocaulacee *Stereocaulon corticatulum* Nyl. v. *procerum* Lamb (called *S. corticulatum* in their publication), but no other reports on the occurrence of parietin in lichens outside Teloschistaceae have been established. In two recent papers,[2-3] parietin was reported in some species usually included in the family Lecideaceae.[4] Santesson found it[3] together with emodin (II) in *Protoblastenia testacea* and *P. rupestris*, while Culberson and Culberson reported it[2] from the latter species and from three *Lopadium* (sens. lat.) species. However, all these species belong to Teloschistaceae.[5]

During a study of anthraquinones in Teloschistaceae,[6] it was considered to be of interest to check whether parietin is, in fact, confined to this family.

RESULTS AND DISCUSSION

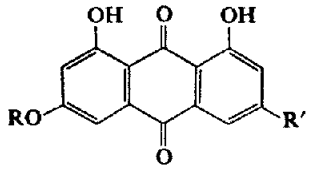
A re-investigation of *Stereocaulon corticatulum* v. *procerum* was carried out, using both an isotype specimen and a duplicate sample of the originally investigated material (later determined by I. M. Lamb as *Leprocaulon tenellum*), but no parietin could be detected. In view of the reported[1] low yield (0·02%) of parietin, its presence as a small impurity in the investigated material cannot be ignored.

However, parietin does occur outside Teloschistaceae. TLC and "lichen mass spectrometry"[3] (LMS) of the orange-coloured *Pyrenula cerina* Eschw. (Pyrenulaceae) indicated the

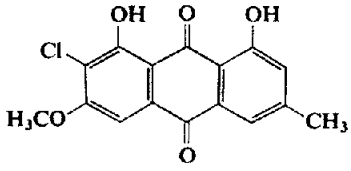
* Part XXVI in the series "Chemical studies on lichens"; for Part XXV see G. BOHMAN, *Tetrahedron Letters*, 445 (1970).

† Outside lichens, parietin has been found, e.g. in *Penicillium, Aspergillus, Cassia, Polygonum, Rhamnus, Rheum,* and *Rumex.*

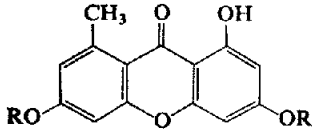
[1] S. HUNECK and G. FOLLMANN, *Z. Naturforsch.* **20b**, 1012 (1965).
[2] C. F. CULBERSON and W. L. CULBERSON, *Bryologist* **72**, 210 (1969).
[3] J. SANTESSON, *Arkiv. Kemi.* **30**, 369 (1969).
[4] M. E. HALE, JR., *The Biology of Lichens*, Arnold, London (1967).
[5] R. SANTESSON, to be published.
[6] R. SANTESSON and J. SANTESSON, to be published.



Parietin (I) R = CH_3, R′ = CH_3
Emodin (II) R = H, R′ = CH_3
Fallacinol (III) R = CH_3, R′ = CH_2OH
Fallacinal (IV) R = CH_3, R′ = CHO



Fragilin (V)



Lichexanthone (VI) R = CH_3
Norlichexanthone (VII) R = H

presence of parietin, which was then isolated in 1% yield and identified by comparison with an authentic sample.

In the apothecia of both *Biatorella conspersa* (Fée) Vain. and *B. ochrophora* (Nyl.) Arn. (Acarosporaceae), parietin was demonstrated by means of TLC and LMS and, in the former species, also by isolation. Also *Arthonia elegans* (Ach.) Almqu. (Arthoniaceae) contains the same anthraquinone together with small quantities of emodin (II), fallacinol (or teloschistin) (III) and fallacinal (IV), the two latter pigments only identified by LMS.

However, in a number of other *Arthonia* species with red apothecia, turning reddish violet upon application of aq. KOH, no parietin could be found. In these cases the pigmentation and the colour reaction are probably caused by another unidentified anthraquinone, not closely related to parietin.

It was suggested by Bohman[7] on the basis of a published mass spectrum[8] that a sample of fragilin (V), isolated from *Sphaerophorus fragilis* (L.) Pers. (Sphaerophoraceae) contained parietin as an impurity. Although it was not explicitly stated, this implies that *S. fragilis* should contain parietin; this was verified by TLC. Furthermore, parietin occurs in two *Trypethelium* (Pyrenulaceae) species: *T. aeneum* (Eschw.) Zahlbr. and *T. aureomaculatum* (Vain.) Zahlbr. Parietin was isolated from both, while the presence of emodin, fallacinol and fallacinal in the former species was demonstrated by LMS. The latter species contains in addition to parietin, lichexanthone (VI) and norlichexantone (VII) as well. The identity of the xanthones was ascertained by isolation and comparison with authentic samples.

VI is fairly common in lichens,[9] but VII has only been found in two *Lecanora* species.[10-11] However, since VII is a likely precursor of VI, their joint occurrence in *T. aureomaculatum* cannot be considered remarkable.

The above results firmly establish the occurrence of parietin in lichens outside Teloschistaceae. Furthermore, many of these parietin-containing species are completely unrelated and

[7] G. BOHMAN, *Arkiv. Kemi.* **30**, 217 (1969).
[8] T. BRUUN, D. P. HOLLIS and R. RYHAGE, *Acta Chem. Scand.* **19**, 839 (1965).
[9] J. SANTESSON, *Acta Univ. Upps., Abstr. Upps. Diss. Sci.* **127**, 1 (1969).
[10] J. SANTESSON, *Acta Chem. Scand.* **22**, 1698 (1968).
[11] J. SANTESSON, *Arkiv. Kemi.* **30**, 461 (1969).

represent several different orders. However, these are only isolated occurrences, and hence they do not reduce the taxonomic value of the presence of parietin for the delimitation of the family Teloschistaceae.

EXPERIMENTAL

Mass spectra were recorded with an LKB 9000 mass spectrometer—gas chromatograph, using the direct inlet system (ion source temp. 270°, ionizing current 60 μA). TLC, including preparative TLC, was carried out on Eastman "Chromatogram" plates (6060, silica gel), using mainly solvent systems previously described.[7,12] The best separation of parietin and fragilin was obtained with petrol. ether (60–70°)–$CHCl_3$ (3:1) and four successive developments.

The lichen material. Voucher specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS), except for the duplicate specimen of *Stereocaulon corticatulum* v. *procerum* which is deposited in the herbarium of the Botanical Museum, Lund (LD). *S. corticatulum* v. *procerum*: (isotype) from Argentina, collected in 1950, reference designation Lamb 6086; (dupl. specimen) Chile, 1965, Follmann 14825-L. *Pyrenula cerina*: (A) Ecuador, Galapagos Isl., 1964, Lich. exs. Colo. 146; (B) Cuba, no year, Wright Lich. exs. Cubae II:643; (C) Cuba, no year, Wright Lich. exs. Cubae II:644. *Biatorella conspersa*: (A) Brazil, no year, E. Warming; (B) Cuba, no year, Wright Lich. exs. Cubae 224. *B. ochrophora*: Sweden, 1969, Tibell 3820. *Sphaerophorus fragilis*: Norway, 1967, J. Sant. *Trypethelium aeneum*: (A) Cuba, no year, Wright Verr. Cubae 160a; (B) Brazil, 1894, Malme 2693 A. *T. aureomaculata*: Brazil, 1885, Wainio Lich. Bras. Exs. 1473.

Stereocaulon corticatulum v. *procerum.* Both the isotype and the dupl. specimen were treated in the same way. Dry lichen (5–7 mg) was extracted with acetone (1 ml). After centrifugation, the extract was evaporated and the residue treated with aq. $NaHCO_3$ and ether. The ether solution was evaporated in a sample tube, which was introduced into the mass spectrometer. No peak at *m/e* 284 was obtained. Had 0·1 μg (0·02 per cent) of parietin been present, a strong peak would have been expected.

Pyrenula cerina. TLC and LMS of samples A, B, and C showed the presence of parietin in all three samples. They were pooled and the material (120 mg) was continuously extracted with $CHCl_3$ for 2 days. The part of the extract insoluble in 0·1 M Na_2CO_3 but soluble in 0·1 M NaOH was crystallized from acetic acid, affording parietin (1·5 mg), m.p. 202–204° (lit.[13] 206–207°), identical (mass and i.r. spectra) with an authentic sample.

Biatorella conspersa and *B. ochrophora.* In sample A and B of *B. conspersa* and in *B. ochrophora* parietin was identified by TLC and LMS. A few apothecia (< 1 mg) from sample B of *B. conspersa* were extracted with $CHCl_3$. Preparative TLC afforded parietin, identified by comparison (mass spectra) with an authentic sample.

Sphaerophorus fragilis. Parietin and fragilin were identified by TLC (co-chromatography).

Trypethelium aeneum. LMS, sample A: Peaks at *m/e* 284-relative intensity 100 per cent (parietin), 270–5 per cent (emodin), 300–5 per cent (fallacinol), and 298–4 per cent (fallacinal); sample B: 284–100 per cent, 270–3 per cent, 300–2 per cent, and 298–1 per cent. In both samples parietin was also identified by TLC. Preparative TLC of an acetone extract of sample B (1 cm^2) yielded parietin, identified by comparison (mass spectra) with an authentic sample.

T. aureomaculata. The presence of parietin, lichexanthone and norlichexanthone was demonstrated by TLC and LMS. Preparative TLC of an acetone extract afforded the same compounds, identified by comparisons (mass spectra) with authentic samples.

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[12] J. SANTESSON, *Acta Chem. Scand.* **21**, 1162 (1967).

[13] Y. ASAHINA and S. SHIBATA, *Chemistry of Lichen Substances*, Japan Society for the Promotion of Science, Tokyo (1954).