

that there is no deviation from eqn. 5 even at this relatively high concentration.

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Chemical Studies on Lichens

28.* The Pigments of Some Foliicolous Lichens

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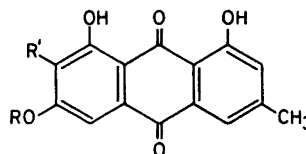
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Nine species of obligately foliicolous lichens have been studied with regard to their content of coloured secondary metabolic products. Three anthraquinones, three pulvinic acid derivatives, three chlorinated xanthenes, and usnic acid were identified by lichen mass spectrometry and thin layer co-chromatography.

The secondary metabolic products of obligately foliicolous lichens (*i.e.* lichens only occurring on living leaves)¹ are virtually unknown. Only one substantiated report on their constituents has appeared in the literature: the occurrence of 2,5,7-trichloronorlichexanthone in *Sporopodium phyllocharis* (Mont.) Mass. and of 3-O-methyl-2,5,7-trichloronorlichexanthone in *S. phyllocharis* var. *flavescens* R. Sant.²

By means of lichen mass spectrometry (LMS)³ and instant thin layer co-chromatography (ITLC)⁴ the pigments of nine foliicolous lichens have been studied. All investigated species belong to the family Lecideaceae.

The impossibility of obtaining more than a few milligrammes of lichen material (in advantageous cases!) has precluded isolation of the substances present and has

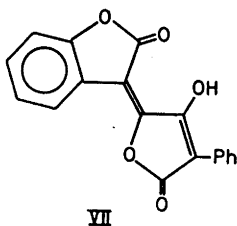
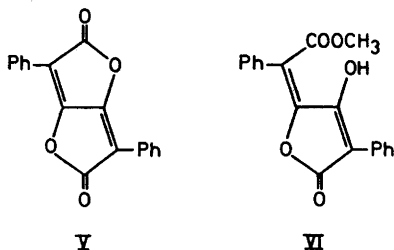


	R	R'
I:	H	H
II:	H	Cl
III:	CH ₃	Cl
IV:	CH ₃	H

* Part 27: Persson, B. and Santesson, J. *Acta Chem. Scand.* **24** (1970) 345.

made it necessary to rely upon LMS and ITLC for the identifications. Both methods have been used in all cases.

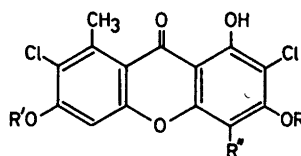
Byssoloma tricholomum (Mont.) Zahlbr. em. R. Sant. was found to contain the closely related anthraquinones emodin (I), 7-chloroemodin (II), and fragilin (III). I–III are rather common within the family Teloschistaceae^{5,6} and scattered occurrences in lichens belonging to other families have also been reported.^{3,7–9} It is significant that no traces of parietin (IV) could be found in *B. tricholomum*. A joint occurrence of I–IV has never been reported from lichens outside Teloschistaceae.



In *Sporopodium leprieurii* Mont. var. *citrinum* (Zahlbr.) R. Sant. and in *S. xantholeucum* (Müll. Arg.) Zahlbr. the presence of the pulvinic acid derivatives pulvinic dilactone (V) and vulpinic acid (VI) could be demonstrated. The latter species was also found to contain calycin (VII). These compounds are not uncommon in lichens (for their distribution see Culbertson¹⁰). It should be noted that typical *S. leprieurii* does not contain any pulvinic acid derivatives.⁹

Five *Lopadium* species have been studied. *L. foliicola* (Fée) R. Sant., *L. fuscum* Müll. Arg., *L. nymanii* R. Sant., and *L. phyllogenum* (Müll. Arg.) Zahlbr. were found to contain 2,7-dichlorolichexanthone

(VIII), previously known only from *Buellia* and *Pertusaria* spp.^{3,11} The same xanthone is also present in some corticolous *Lopadium* spp.⁶ It should be noted that the four foliicolous *Lopadium* spp. containing VIII all belong to the *L. fuscum* group.¹



	R	R'	R''
VIII:	CH ₃	CH ₃	H
IX:	H	H	Cl
X:	CH ₃	H	Cl

In *L. newtonianum* (Henriques) R. Sant., the presence of usnic acid was demonstrated. Usnic acid is very common in lichens.

Finally, *Tapellaria epiphylla* (Müll. Arg.) R. Sant. was shown to contain the chlorinated xanthenes arthothelin (IX) and thuringione (X). IX is fairly common in lichens,³ while X has been found only in one *Lecanora* sp.,³ one *Buellia* sp.,² and one *Lecidea* sp.¹²

Experimental. The lichen mass spectra were recorded according to Ref. 3, using an LKB 9000 gas chromatograph–mass spectrometer, equipped with a direct inlet system. TLC identifications were made by co-chromatography with authentic samples on Eastman “Chromagram” plates (6060, silica gel), using solvent systems previously described.^{4,11,13}

The lichen material. Voucher specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS). *Byssoloma tricholomum*: from Cuba, unknown year of collection, reference designation Wright, Lich. Cuba II, 200. *Sporopodium leprieurii* var. *citrinum*: China, 1916, Handel-Mazzetti 9866 (isotype). *S. xantholeucum*: New Guinea, 1929, Herre. *Lopadium foliicola*: Brazil, 1892, Malme 376 a. *L. fuscum*: New Guinea, 1940, Clemens. *L. nymanii*: Java, 1897, Nyman E L 11 a (holotype). *L. phyllogenum*: Brazil, 1894, Malme 2398. *L. newtonianum*: São Thomé, 1888, Newton (isotype). *Tapellaria epiphylla*: Brazil, 1880, Puiggari 1086 (isotype).

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The Single and Double Bonds between sp^2 -Hybridized Carbon Atoms, as Studied by the Gas Electron Diffraction Method

VI. The Molecular Structure of Acrolein

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The molecular structure of acrolein is a natural choice for inclusion in the present research series. The molecular structure of this molecule was studied by microwave spectroscopy in 1966¹ and more recently by electron diffraction.² When the latter results appeared, however, the experimental part of the investigation reported here was already carried out, and it was decided to continue the structure study. Even if the structural results may be of somewhat reduced interest, it might be worth while to compare results obtained by different electron diffraction laboratories.

The experimental data for the electron diffraction study of acrolein were recorded at two camera distances, approximately 48 cm and 19 cm. The data were combined to give an experimental molecular intensity function ($sM(s)$ -function) in the s -range 1.25–45.0 Å⁻¹. The molecular structure was studied by least squares refinements of the experimental molecular intensity function and by following the progress on radial distribution functions. In the structure analysis all C=C—H angles were assumed to be equal and the CH bond distance in the aldehyde group was assumed to be 0.02 Å larger than the other CH bond distances.

Table 1 lists the final results for the internuclear distances and mean amplitudes of vibrations for acrolein. The distances are arranged in order of increasing internuclear distance so that it will be easy to identify them in Figs. 3 and 4 which show the experimental and theoretical radial distribution functions when two different damping constants are applied. The solid bars represent relative contributions from the internuclear distances listed in Table 1.