

exactly a third of the total radioactivity of the malonate which is only compatible with the formation of malonate exclusively by oxidative α -decarboxylation, *i.e.* according to route 1 or 2. In the second experiment using uniformly labelled aspartate a slightly higher radioactivity was obtained in the methylene group as compared to the radioactivity of each carboxyl group which might indicate some contribution of route 4 to the malonate formation. Calculations from the figures in the table show that 77 % of the labelling in the malonate is derived from route 1 or 2 and 23 % from route 4.

The experiments demonstrate thus that there is a metabolic pathway in *P. islandicum* from oxalacetate to malonate in which oxidative α -decarboxylation of oxalacetate is involved. The question whether this reaction is related to the oxidative decarboxylation of pyruvate or is of peroxidase character can only be settled when the reaction is studied in a cell free system.

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Chemical Studies on Lichens

12.* A New Lichen Xanthone from

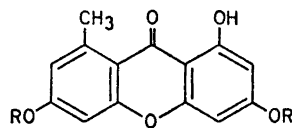
Lecanora reuteri

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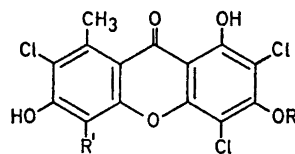
A rapidly growing number of xanthenes, most of which chlorinated, are known from lichens. Some examples are lichexanthone (II),¹ thiophanic acid (III),²⁻⁴ arthothelin (IV),⁵⁻⁷ and thuringion (V).⁷⁻⁸ All these are derived from the same parent compound norlichexanthone (I, 1,3,6-trihydroxy-8-methylxanthene-9H-9-one).

During a screening of *Lecanora* species by "lichen mass spectrometry"⁸ it was found that the spectrum of *L. reuteri* Schaer. (Fig. 1) exhibited a strong peak at *m/e* 258 which suggested the presence of norlichexanthone (*M*=258). A peak at *m/e* 360 with satellite peaks at *m/e* 362, 364, and 366 indicated the presence of the corresponding trichlorinated xanthone arthothelin (IV).



I R = H

II R = CH₃



III R = H R' = Cl

IV R = R' = H

V R = CH₃ R' = H

* Part 11. *Arkiv Kemi. In press.*

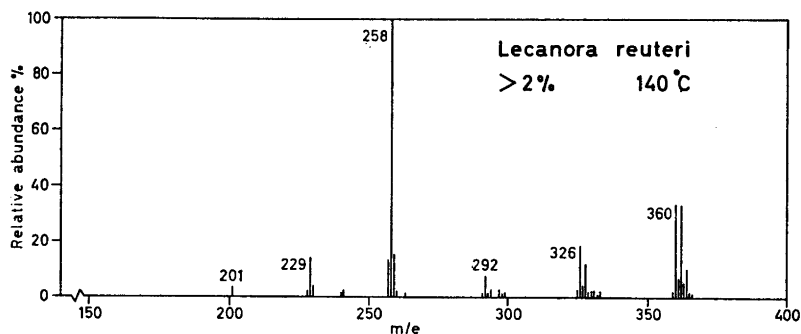


Fig. 1.

These tentative identifications were verified by isolation of the compounds and comparison with authentic specimens.

Norlichexanthone has previously not been found in Nature. It has been prepared as an intermediate in the synthesis of lichexanthone¹ and thiophanic acid.³

Arthothelin is known from *Arthothelium pacificum* Follm.,⁵ *Lecidea querneae* (Dicks.) Arn.,⁸ and some *Lecanora* species.⁶⁻⁷

Experimental. Lichen samples: *Lecanora reuteri* (A) from Unterwalden, Switzerland, reference designation R. Sant. 1946; (B) Jura, Switzerland, Frey 1929. Specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS).

Dry and ground lichen (sample A, 1.2 g) was extracted with acetone (20 ml, 12 h), the solution concentrated to 5 ml, and ether (20 ml) added. This solution was extracted with sodium hydrogen carbonate solution (5%, 2 × 5 ml) and then with sodium carbonate solution (10%, 2 × 5 ml).

Acidification of the NaHCO₃ solution (2 N hydrochloric acid), ether extraction, and preparative TLC (silica gel G, dichloromethane-acetone 4:1) afforded arthothelin (IV, 1.1 mg), identified by comparison with an authentic sample (IR spectra, co-chromatography).

Acidification of the Na₂CO₃ solution (2 N hydrochloric acid), ether extraction, and recrystallisation from ethanol-water of the residue obtained after evaporation of the

ether, yielded norlichexanthone (I, 3.0 mg), m.p. 272–74°, identified by comparison with a synthetic³ sample (IR, mixed m.p.'s).

In an acetone extract of the lichen (sample B), I and IV were identified by co-chromatography (TLC according to Ref. 9) with authentic samples.

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