- Hultquist, D. E. Biochim. Biophys. Acta 153 (1968) 329.
- Zetterqvist, Ö. Biochim. Biophys. Acta 141 (1967) 523.
- Koshland, D. E., Jr. J. Am. Chem. Soc. 74 (1952) 2286.
- Herr, E. B., Jr. and Koshland, D. E., Jr. Biochim. Biophys. Acta 25 (1957) 219.

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The Occurrence of Atranorin in Letharia vulpina (L.) Vain.

TORGER BRUUN and NILS ANDREAS SØRENSEN

Institutt for organisk kjemi, Norges tekniske høiskole, N-7034 Trondheim-NTH, Norway

At an altitude of 6500-7500 ft the dense and umbrageous forests of Yosemite National Park, California, USA, are decorated by 1/2-1 ft long tails of a golden coloured lichen. During an accidental visit to the park one of us (N.A.S.) collected some large specimens from the surroundings of Glacier Point and Mariposa Grove, where this lichen is very abundant. Most of this material was subjected to a chemical examination, whilst a small specimen was sent to Professor Eilif Dahl for determination. Dr. Dahl kindly informed us that the lichen was Letharia vulpina, a lichen which is not unknown in Southern Norway, although it is usually of a much smaller size. The Scandinavian L. vulpina occurs as 1-2 inch asymmetrical tufts on wooden roofs, fences and the like. As far as we know it does not occur as free-hanging, long tails under shading twigs in the way typical of some Scandinavian Alectoria species. The distribution of L. vulpina in Scandinavia is restricted to a small area with a pronounced continental climate, and its local occurrence to very open places.

In agreement with literature 'vulpinic acid was found as the major constituent, but in addition a small amount of colourless crystals was seen. Eventually they were identified with atranorin. For details, see Experimental.

Atranorin is a very common lichen acid,¹ but to our knowledge it has not previously been found in lichens producing vulpinic acid type substances.

The possibility existed that *L. vulpina* growing in North America might be different in acid content from *L. vulpina* growing in Scandinavia. To test this possibility a sample of the lichen was obtained from Höljes, Sweden. Atranorin was found as in the North American sample. Thus, although the two types of *L. vulpina* differ remarkably in both morphology and ecology, they agree as far as the dominating lichen acids are concerned.

Experimental. Air dried and ground L. vulpina (64 g) collected under Abies magnifica Murr. was extracted with ether for 24 h in a Soxhlet extractor. On thin layer chromatograms on silica gel in benzene-chloroform 1:1 and anisaldehyde as spraying agent ² several spots were obtained. Two of them were identified as due to the presence of vulpinic acid and of atranorin.

The ether solution was concentrated twice to deposit a mixture of coloured and colourless crystals. The coloured crystals were removed by hand, whilst the colourless crystals remained. The former were shown to be identical with vulpinic acid by comparison with an authentic sample. The latter were crystallised from acetone, m.p. 194–195° (108 mg). The material gave a negative Beilstein test, and there was no depression of m.p. on admixture with authentic atranorin. Their IR spectra in KBr, obtained with a Perkin-Elmer Model 21 spectrometer, were essentially identical.

A sample of *L. vulpina* from Höljes, Sweden, (36 g) was treated as above, except that vulpinic acid was removed by treatment with chloroform in the cold. Colourless crystals (11 mg) remained on the filter, m.p. 193-194° after one crystallisation from acetone. There was no depression on admixture with authentic atranorin and the IR spectra in KBr were essentially identical.

We are grateful to Dr. Eilif Dahl for the determination of the lichen, to Mr. A. Opperud, Deje, Sweden, who arranged the collection, and to Mr. L. Törnskog, Höljes, Sweden, who did the collection of *L. vulpina*.

- Asahina, Y. and Shibata, S. Chemistry of Lichen Substances, Japan Society for the Promotion of Science, Tokyo 1954.
- Stahl, E. and Schorn, P. J. Z. physiol. Chem. 325 (1961) 263.

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