

Chemical Studies on Lichens

2.* Thin Layer Chromatography of Aliphatic Lichen Acids

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The only general method hitherto described for separation and identification of aliphatic lichen acids is the micro-crystallisation method of Asahina.¹ However, this method does not seem to be quite reliable for determination of aliphatic acids, especially when more than one acid is present in the lichen species. In the present paper a method of separating some aliphatic lichen acids by thin layer chromatography is presented. The results are summarized in Table 1. For system A the variations in the R_F -values might amount to ± 0.05 but the sequence of the acids is always the same. All known lichen acids containing a γ -lactonic group except allo-protolichesterinic acid, which was not

available, have been investigated. Two pairs of homologous acids (nephrosterinic acid and protolichesterinic acid; nephromopsinic acid and nephrosteranic acid) were not resolved by any of the solvent systems tried.

By means of these solvent systems we have also been able to prove that the "Pleopsidsäure" described by Zopf² is a mixture of two acids. These acids we have named acaranoic acid and acarenoic acid (after the lichen genus *Acarospora*) and their structures will be described in a future publication.

Experimental. The thin layer chromatography was carried out according to Stahl.³ Silica gel HF was used as adsorbant. A solution of 40 mg bromo cresol green in 100 ml 0.01 N NaOH was used as indicator spray.

Caperatic acid was isolated from *Parmelia caperata* (L) Ach., protolichesterinic acid from *Cetraria islandica* (L) Ach., and rangiformic acid from *Cladonia rangiformis* Hoffm. Nephromopsinic acid was obtained from *Nephromopsis stracheyi* (Bab.) Müll. Arg. f. *ectocarpisma* Hue (leg. Kurokawa No. 56318) by preparative thin layer chromatography in solvent system A. Lichesterinic acid was synthesised from protolichesterinic acid as described by Zopf.⁴ Norrangiformic acid was obtained by alkaline hydrolysis of rangiformic acid. Nephrosteranic and nephrosterinic acids were put at our disposal by Professor S. Shibata, Tokyo. Roccellic acid was obtained from *Rocella fucooides* (Dicks.) Vain., and acaranoic acid and acarenoic acid were prepared as a mixture ("Pleopsidsäure") according to Zopf² from *Acarospora chlorophana* (Wg) Mass. and separated by preparative thin layer chromatography in solvent system A.

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Table 1.

Compound	$R_F \times 100$ in solvent system			
	A	B	C	D
Caperatic acid	03	02	01	11
Lichesterinic acid	73	32	56	×
Nephromopsinic acid	82	32	54	×
Nephrosteranic acid	82	31	55	×
Nephrosterinic acid	61	22	43	×
Norrangiformic acid	04	03	03	49
Acaranoic acid	68	26	42	×
Acarenoic acid	48	17	30	×
Protolichesterinic acid	61	23	43	×
Rangiformic acid	50	10	36	66
Roccellic acid	91	24	60	×

× = the acid travels with the secondary front

A: ether-butyric acid 20:1 (v/v)

B: chloroform-propionic acid 20:1 (v/v)

C: isopropyl ether-propionic acid 20:1 (v/v)

D: chloroform-acetic acid 5:1 (v/v)

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