

Chemical Studies on Lichens

6.* The Chemistry of the Genus *Siphula*. II

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Ten *Siphula* species have been studied with regard to their contents of "lichen substances". Porphyrilic acid, strepsilin, baeomycesic acid, squamatic acid, thamnolic acid, decarboxythamnolic acid, barbatic acid, atranorin, chloroatranorin, and norstictic acid have been isolated or identified chromatographically. In two species, siphulitol has been demonstrated.

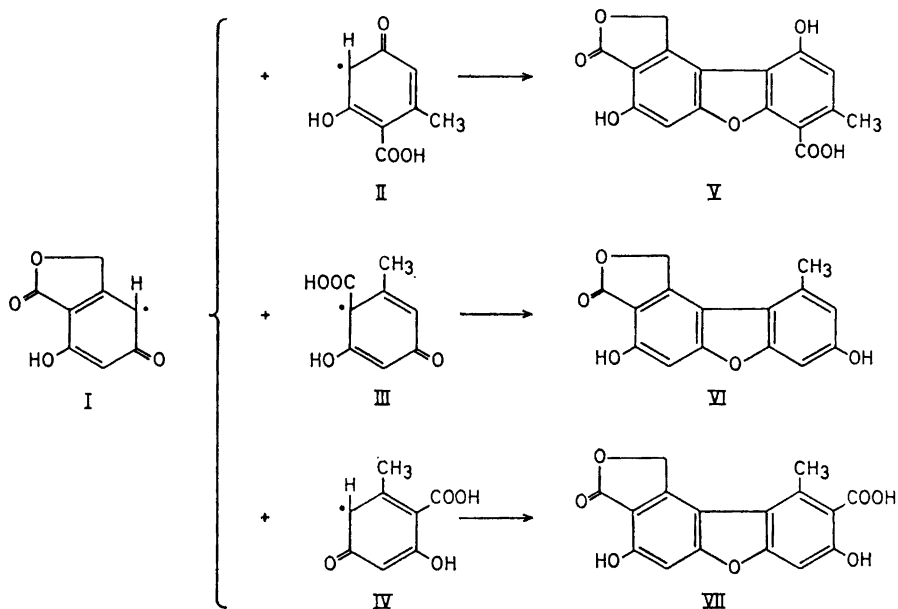
In a previous communication¹ the investigation of seven *Siphula* species with regard to their contents of aromatic acids was reported. Hypothamnolic acid was found in three species, baeomycesic and squamatic acid in three other species, and finally thamnolic and decarboxythamnolic acid in one species.

We have now studied ten more *Siphula* species. The results are summarized in Table 1. *S. comata* (Nyl.) R. Sant. is not included in the table, since no lichen substances were found. The compounds were identified by comparison with authentic samples. In most cases, this was effected by co-chromatography according to Santesson,² but in some cases the compounds were isolated to obtain more reliable identification (IR spectra, mixed m.p.'s, etc.).

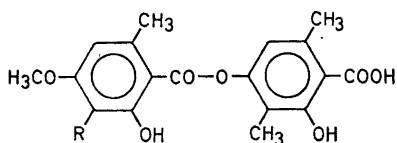
The joint occurrence of porphyrilic acid (V) and strepsilin (VI) in *S. complanata* is of special interest. Wachtmeister suggested³ that lichen dibenzofuranes are formed by coupling of simple phenolic radicals. Thus I + II would give rise to porphyrilic acid (V), whereas I + III would result in strepsilin (VI) (after decarboxylation of the intermediate).

The occurrence of both V and VI in the same lichen suggests a certain lack of specificity in the enzyme system present, that controls the coupling step. However, there is no evidence whatsoever for the presence of VII, which would arise from I + IV. This unknown compound would be expected if the coupling was completely uncontrolled. As a contrast to *S. complanata*, *S. nepalensis* contains porphyrilic acid alone.

* Part 5: *Acta Chem. Scand.* 21 (1967) 1376.



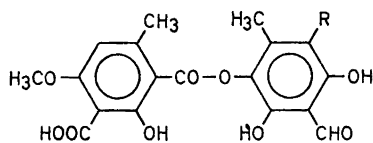
Porphyrilic acid has previously been isolated from *Haematomma coccineum* (Dicks.) Körb. var. *coccineum*^{4,5} and var. *porphyricum* (Pers.) Th. Fr.⁴ and also from *Lecidea silacea* (Ach.) Ach.⁶ Strepsilin is only known from *Cladonia strepsilis* (Ach.) Vain.⁷⁻⁹ where it occurs together with baemycesic and squa-



VIII: R = CH₃

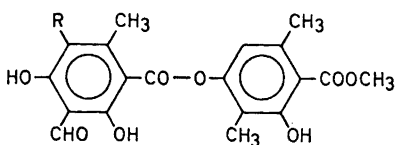
IX: R = CHO

X: R = COOH



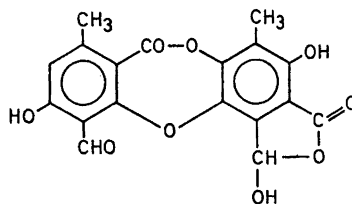
XI: R = COOH

XII: R = H



XIII: R = H

XIV: R = Cl



XV

Table 1.

	Baeomycesic acid (IX) Squamatic acid (X)	Thamnolic acid (XI) Decarboxythamnolic acid (XII)	Barbatic acid (VIII)	Porphyritic acid (V) Strepsilin (VI)	Atranorin (XIII) Chloroatranorin (XIV)	Norstictic acid (XV) Unidentified comp.
<i>S. applanata</i> H. Magn.	+ +					
<i>S. subulata</i> Krempelh.	+ +					
<i>S. polyschides</i> Krempelh.	+ +				+ +	
<i>S. carassana</i> Müll. Arg.		++ (+)				+
<i>S. dichotoma</i> Vain.		+ (+)				
<i>S. coriacea</i> Nyl.			+			
<i>S. complanata</i> (Hook. f. et Tayl.) R. Sant.				++ ++		
<i>S. nepalensis</i> R. Sant. sp. n.				++		
<i>S. dactyliza</i> Nyl.					+ +	+

+ = Identified chromatographically.
 (+) = " " but only as traces.
 ++ = Isolated.

matic acid.⁸⁻⁹ The report that *C. strepsilis* also should contain thamnolic acid has not been confirmed.^{8,10}

Baeomycesic acid is known from *Baeomyces* sp., *Thamnotia* sp.,¹¹ and *Cladonia* sp.,¹² and *Siphula* sp.¹ Squamatic acid has been found in *Thamnotia* sp., *Cladonia* sp.,¹¹ and *Siphula* sp.¹ Thamnolic and barbatic acid are fairly widespread, e.g. in *Cladonia*.¹¹ The same holds true for norstictic acid, atranorin, and chloroatranorin.

From *S. ceratites*, Lindberg and Meier¹³ isolated a new heptitol, siphulitol. A paper chromatographic investigation of the water-soluble parts of the acetonic extracts of *S. complanata* and *S. fastigiata* (Nyl.) Nyl. var. nov.

revealed the presence of siphulitol, together with mannitol and arabinitol. The two latter compounds are common in lichens.¹⁴ The occurrence of siphulitol may possibly have a taxonomic significance (*cf.* Refs. 14, 15).

EXPERIMENTAL

All melting points are uncorrected. The thin layer chromatography was carried out according to Santesson² on Eastman "Chromagram" K 301 R2, the paper chromatography as described by Lindberg and Meier.¹⁵ The IR spectra were recorded on a Perkin-Elmer 157 (KBr discs).

The lichen material. Voucher specimens are to be found in the herbarium of Uppsala Botanical Museum (UPS). *S. appplanata* from Hawaii, collected in 1938, quotation number Skottsberg 5760; *S. subulata*, Hawaii, 1938, Skottsberg 5612; *S. polyschides*, Hawaii, 1948, Skottsberg 7065; *S. carassana*, Venezuela, 1962, S. Nilsson s.n.; *S. dichotoma*, Borneo, before 1922, nat. coll. 1216; *S. coriacea*, Australia, 1947, Burbridge; *S. complanata* (1), Chile, 1929, Roivainen 23. II. 29; *S. complanata* (2), Tasmania, 1963, PW James AU 2080; *S. nepalensis*, Nepal, 1954, Stainton 6349; *S. dactyliza*, USA (Alaska), 1932, E. Hultén 9. VIII. 32; *S. comata*, Chile, 1868, Cunningham; *S. fastigiata*, Argentine, 1940, R. Sant. 480.

Reference compounds. All reference compounds but decarboxythamnolic acid and siphulitol are from the sources given in Ref. 2. Decarboxythamnolic acid was synthesized from thamnolic acid according to Asahina *et al.*¹⁶ Siphulitol was obtained from *S. ceratites*.¹³

Chromatographic procedure. The dry, ground lichen (5–50 mg) was extracted with hot acetone (2 × 0.3 – 2 × 1.5 ml) in a test tube. The combined, filtered, and concentrated (0.1 – 0.5 ml) extracts were used for thin layer chromatography. Identification was effected by co-chromatography with reference compounds.

Thamnolic acid. *S. carassana* (85 mg) was extracted continuously with acetone (5 ml) over night. Concentration of the extract (0.2 ml) yielded crystals, which were recrystallized from dioxane. The substance thus obtained (1.2 mg, 1.4 %), m.p. 217–219°, was proved to be identical with thamnolic acid (IR, mixed m.p.).

Porphyrylic acid and strepsilin. Dry *S. complanata* (1) (315 mg) was extracted continuously with acetone (15 ml) for 48 h. The acetone was evaporated and water (0.5 ml) added to the dry extract. After 24 h, the insoluble residue was removed by centrifugation. The supernatant liquid was used directly for the paper chromatographic detection of polyols. The residue was extracted with sodium hydrogen carbonate-sodium hydroxide buffer (pH 9.2, 5 × 2 ml) at room temperature. Acidification with dilute hydrochloric acid of the combined extracts yielded a precipitate (A).

The part insoluble in the above buffer solution was extracted with sodium carbonate-sodium hydroxide buffer (pH 11.8, 5 × 2 ml) at 0°. Acidification of the combined extracts with dilute hydrochloric acid yielded a precipitate (B).

The precipitate A was recrystallized from ethanol, affording a substance (3.0 mg, 1.0 %) m.p. 271–275° (decomp.), identical with porphyrylic acid (mixed m.p., IR). To ensure complete identification, it was converted to methyl *O*-dimethyl porphyrilate as described by Wachtmeister.⁵ The product was identical (IR, mixed m.p.) with a specimen synthesized from authentic porphyrylic acid.

Recrystallisation of precipitate B from glacial acetic acid yielded a substance (2.8 mg, 0.9 %) m.p. 318–321°, which was proven identical with strepsilin (IR, mixed m.p.).

Treated as above, *S. complanata* (2) (345 mg) afforded porphyrylic acid and strepsilin in comparable yields. *S. nepalensis* (75 mg) yielded only porphyrylic acid (0.9 mg, 1.2 %), identified by IR and mixed m.p.

Siphulitol. *S. fastigiata* (125 mg) was extracted continuously with acetone (10 ml) for 48 h, the acetone was evaporated and the residue treated with water (0.2 ml) for 24 h. After centrifugation, the supernatant water solution was used for paper chromatography, as were the corresponding solutions from the *S. complanata* extractions (*vide supra*). In all three, siphulitol, mannitol, and arabinitol were identified by co-chromatography.

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