dimer and the mechanism for the dimerisation is under investigation.

\[
\begin{align*}
\text{R}_1 & = \text{CH}_3, \text{R}_2 = \text{H} \\
\text{II} & = \text{R}_1 = \text{t}-\text{Bu}, \text{R}_2 = \text{H} \\
\text{III} & = \text{R}_1 = \text{R}_2 = \text{CH}_3
\end{align*}
\]

Experimental. 2-Methyl-3-hydroxythiophene. 49 g of butyl borate in 150 ml absolute ether was added in a single portion to 2-methyl-3-thienyllithium which had been prepared from 160 ml 1.05 N butyllithium and 25.6 g (0.15 mole) of 2-methyl-3-bromothiophene in 100 ml absolute ether at -70°C. The mixture was stirred at -60° for 4 h and then allowed to warm slowly to 0°. The reaction mixture was decomposed with 120 ml of cold 2 N hydrochloric acid. The aqueous layer was extracted twice with ether and the combined ethereal phases were extracted with 100 ml of cold 2 N sodium hydroxide solution. Acidification of the alkaline solution with cold 2 N sulphuric acid gave the boronic acid which was immediately dissolved in ether.

90 ml of 10% hydrogen peroxide solution was added with stirring at room temperature to the ethereal boronic acid under nitrogen. When the addition was complete the mixture was refluxed for half an hour and after cooling the layers were separated. The water layer was extracted with ether and the combined ethereal phases were washed five times with 15 ml portions of cold water, or until the water phase did not oxidize ferrous ammonium sulphate, and dried over magnesium sulphate. Distillation \textit{in vacuo} under nitrogen yielded 8.3 g (49%) of the tautomeric 2-methyl-3-hydroxythiophen (I) b.p. 92°/12 mm Hg, 1\textsubscript{D} = 1.5460. \textit{Acetate} b.p. 86°/10 mm Hg, 1\textsubscript{D} = 1.5123. (Found: C 53.60; H 5.08; S 20.33. Calc. for \text{C}_7\text{H}_8\text{O}_2\text{S} (156.19): C 53.82; H 5.16; S 20.53.)

The NMR-spectra were recorded in carbon disulphide solution on a Varian Associate model HR 60 high resolution spectrometer.

Acknowledgements. The author wishes to express her sincere thanks to Professor Salo Gronowitz for his interest in this work and for all facilities put at her disposal.

Thanks are also due to Miss Merete Lange for recording the NMR-spectra.

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Studies on the Chemistry of Lichens

22* The Chemistry of the Genus Siphua. I

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The lichen genus \textit{Siphua} has its main distribution in the southern hemisphere although one species, \textit{S. ceratitis}, occurs mainly in northern Scandinavia. The genus consists only of sterile species and hence the taxonomical questions are far from simple. A thorough chemical investigation might therefore, in this case, be of special value. So far, only \textit{S. ceratitis} has been chemically investigated by Bruun and by Lindberg \textit{et al.} Recently Miss Annick Mathey has made an independent investigation of some species belonging to the genus \textit{Siphua} using Asahina’s microcrystallisation method.


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**Table 1.**

<table>
<thead>
<tr>
<th></th>
<th>Hypothannolic acid (I)</th>
<th>Thammolic acid (II)</th>
<th>Decarboxy thammolic acid (III)</th>
<th>Baeomycesic acid (IV)</th>
<th>Squamatic acid (V)</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>S. dissoluta</em> (Nyl.) A. Zahlbr.</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td><em>S. roccelliformis</em> Nyl.</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td><em>S. fastigiata</em> (Nyl.) Nyl. var. nov.</td>
<td>×</td>
<td></td>
<td></td>
<td>×</td>
<td>×</td>
</tr>
<tr>
<td><em>S. decumbens</em> Nyl.</td>
<td></td>
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<tr>
<td><em>S. moorei</em> A. Zahlbr.</td>
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<tr>
<td><em>S. verrucigera</em> (J. F. Gmelin)</td>
<td></td>
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<tr>
<td>R. Sant. (= <em>S. tubularis</em> (Thum. ex Ach.) Nyl.)</td>
<td></td>
<td></td>
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<td></td>
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<tr>
<td><em>S. torulosa</em> (Thum. ex Ach.) Nyl.</td>
<td></td>
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</tr>
</tbody>
</table>

![Chemical structures](image)

We have studied seven *Siphula* species with regard to their contents of aromatic acids. The results are summarized in Table 1. The acids were identified by comparison with authentic specimens, either by infrared spectra and determination of mixed melting points or by chromatography. Hypothannolic acid was identified with reasonable certainty, by colour reactions and by co-chromatography of its hydrolysis products with authentic samples. Since decarboxythannolic acid is often reported to occur together with thammolic acid, it might be possible that it is an artefact.

Hypothannolic acid has previously been reported from *Cladonia pseudostellata*. Thammolic acid, which we have also isolated from *Icmadophil a ericetorum* Cumb. and *Endocena informis* (L.) Zahlbr.,* has been found in *Thannopedia* sp., *Cladonia* sp., *Parmeoliopsis* sp., and *Pertusaria* sp. *Squamatic acid* has been reported from *Cladonia* sp. and *Thannopedia* sp.* *Baeomycesic acid* from *Baeomyces* sp. and *Thannopedia* sp.* The joint occurrence of squamatic and baeomycesic acid is of special interest, since they represent different stages in the oxidation of the same parent depside. The same combination of acids has long been known to occur in *Thannopedia subuliformis.* The presence of these related acids indicates a close relationship between these seven investigated species.

**Experimental.** All melting points are uncorrected. The thin layer chromatography was carried out according to *Stahl,* using silica gel G as adsorbent and benzene-acetic acid-dioxane (90:4:25 v/v/v) as solvent. UV light (365 nm), Echtblaualtz B and p-phenylenediamine were used to reveal the spots.

**The lichen material.** Quotation specimens are to be found in the herbarium of Uppsala Botanical Museum. *Siphula roccelliformis* from New Zealand, South Island, collected in 1927, quotation number Du Rietz 1752:5; *S. dissoluta*, New Zealand, South Island, 1927, Du Rietz 2037:1; *S. fastigiata*, Argentine, Tierra del Fuego, 1940, R. Sant. 480; *S. moorei*, New Zealand, South Island, 1927, Du Rietz.

* Unpublished results.

Thin layer chromatography of the remaining acetic mother liquor showed the presence of baemocystic acid ($R_F = 0.48$), in all respects identical with a co-chromatographed authentic sample.

Dry $S. torulosae$ (0.03 g) was extracted with acetone ($2 \times 0.5$ ml) as above. Thin layer chromatography revealed two main spots ($R_F = 0.28$ and 0.60), in all respects identical with co-chromatographed squamatic acid and baemocystic acid, respectively.

**Thamnolic acid and decarboxythamnolic acid.**

Dry $S. decumbens$ (0.3 g) was extracted with acetone ($3 \times 10$ ml) at 50° for 1 h. Concentration of the combined acetic extracts yielded crystals, which were recrystallised from dioxane. The substance thus obtained (5 mg, 1.7 %), m.p. 221—222°, was proved to be identical with thamnolic acid (mixed m.p., IR).

Thin layer chromatography of the remaining acetic mother liquor revealed a spot ($R_F = 0.50$), in all respects identical with co-chromatographed decarboxythamnolic acid.

**Acknowledgements.** Our thanks are due to Professor Arne Fredga for the facilities put at our disposal and to Dr. Rolf Santesson, who first suggested this investigation, for the generous supply of identified lichen material, and for stimulating discussions.

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