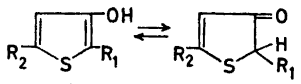
dimer and the mechanism for the dimerisation is under investigation.



I	80	20
II	55	45
III	30	70

I $R_1 = CH_3$, $R_2 = H$
II $R_1 = t\text{-}Bu$, $R_2 = H$
III $R_1 = R_2 = CH_3$

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 26.5 g (0.15 mole) of 2-methyl-3-bromothiophene[7] in 100 ml absolute ether at −70°. 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 *in vacuo* under nitrogen yielded 8.3 g (49 %) of the tautomeric 2-methyl-3-hydroxythiophen (I) b.p. 92−98°/12 mm Hg, $n_D^{20} = 1.5460$. *Acetate* b.p. 86°/10 mm Hg, $n_D^{20} = 1.5123$. (Found: C 53.60; H 5.08; S 20.33. Calc. for $C_7H_8O_2S$ (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.

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

1. Gronowitz, S. and Hoffman, R. A. *Arkiv Kemi* **15** (1960) 499.
2. Hörnfeldt, A.-B. and Gronowitz, S. *Acta Chem. Scand.* **16** (1962) 789.
3. Hörnfeldt, A.-B. and Gronowitz, S. *Arkiv Kemi* **21** (1963) 239.
4. Hörnfeldt, A.-B. *Arkiv Kemi* **22** (1964) 211.
5. Katritzky, A. R. and Lagowski, J. M. *Advan. Heterocyclic Chem.* **2** (1963) 9.
6. Ford, M. C. and Mackay, D. *J. Chem. Soc.* **1956** 4985.
7. Gronowitz, S., Moses, P., Hörnfeldt, A.-B. and Håkansson, R. *Arkiv Kemi* **17** (1961) 165.

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Studies on the Chemistry of Lichens

22* The Chemistry of the Genus *Siphula*. I

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The lichen genus *Siphula* has its main distribution in the southern hemisphere although one species, *S. ceratites*, 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 *S. ceratites* has been chemically investigated by Bruun[1] and by Lindberg *et al.*[2] Recently Miss Annick Mathey has made an independent investigation of some species belonging to the genus *Siphula* using Asahina's microcrystallisation method.[3]

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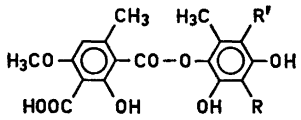
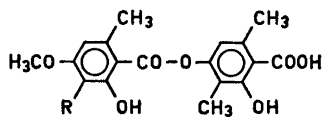
Table 1.

	Hypothamnolic acid (I)	Thamnolic acid (II)	Decarboxy thamnolic acid (III)	Baeomycesic acid (IV)	Squamatic acid (V)
S. dissoluta (Nyl.) A. Zahlbr.	×				
S. roccellaeformis Nyl.	×				
S. fastigiata (Nyl.) Nyl. var. nov.	×				
S. decumbens Nyl.		×	×		
S. moorei A. Zahlbr.				×	×
S. verrucigera (J. F. Gmelin) R. Sant. (= *S. tabularis* (Thunb. ex Ach.) Nyl.)				×	×
S. torulosa (Thunb. ex Ach.) Nyl.				×	×



I: R = CH_3 R' = COOH
II: R = CHO R' = COOH
III: R = CHO R' = H



IV: R = CHO
V: R = COOH

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. Hypothamnolic acid was identified with reasonable certainty, by colour reactions and by co-chromatography of its hydrolysis products with authentic samples. Since decarboxythamnolic acid is often reported to occur together with thamnolic acid,[4] it might be possible that it is an artefact.

Hypothamnolic acid has previously been reported from *Cladonia pseudostellata*.[5] Thamnolic acid, which we have also isolated from *Icmadophila ericetorum* Cromb. and *Endocena informis* (L.) Zahlbr.,* has been found in *Thamnolia* sp., *Cladonia* sp., *Parmeliopsis* sp., and *Pertusaria* sp.[6] Squamatic acid has been reported from *Cladonia* sp. and *Thamnolia* sp.,[6] baeomycesic acid from *Baeomyces* sp. and *Thamnolia* sp.[6]

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 *Thamnolia subuliformis*.[6] 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,[7] using silica gel G as adsorbent and benzene-acetic acid-dioxane (90:4:25 v/v/v) as solvent.[8] UV light (365 mμ), Echtblausaltz 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 roccellaeformis* 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.

1510:2; *S.verrucigera*, South Africa, Cape prov., 1944, Leighton 708; *S. torulosa*, South Africa, Cape prov., 1942, Garside; *S. decumbens*, New Zealand, South Island, 1927, Du Rietz 1812:1.

Reference compounds. Thamnolic acid was isolated from *Pertusaria corallina* (Ach.).[9] Squamatic acid was obtained from *Thamnolia subuliformis* (Ehrh.) W. Culb. according to Asahina and Shibata [10] and baeomycesic acid from the same lichen by means of thin layer chromatography. Decarboxythamnolic acid was synthesized from thamnolic acid according to Asahina *et al.*[11] 1-*O*-Methyl-orcinol-2,4-dicarboxylic acid was obtained from thamnolic acid as described by Asahina *et al.*[12] 2-Methyl-6-hydroxy-orcinol-4-carboxylic acid was synthesized according to Asahina *et al.*[5]

Hypothamnolic acid. A dry sample of *S. roccellaeformis* (1.95 g) was extracted twice with ether (2 × 40 ml) at 20° for 1 h, then three times with acetone (3 × 50 ml) at 20° for 2 h. Upon concentration of the combined acetonic extracts, a crystalline precipitate was obtained which after repeated recrystallisations from 80 % acetone afforded an acid (54 mg, 2.8 %), m.p. 225–227° (decomp.). *S. dissoluta* and *S. fastigiata* were treated in the same way and afforded 2 % and 1 %, resp., of the same acid (mixed m.p., IR). The colour reactions of this acid, *e.g.* the momentary red colour formed with bleaching powder (due to the two free *m*-hydroxyl groups), agreed with those reported by Asahina *et al.*[5] for hypothamnolic acid. The acid (3 mg) was dissolved in ice-cold concentrated sulphuric acid (0.3 ml). After 5 min, the solution was poured into ice water and then extracted with ether. Thin layer chromatography of the ethereal solution revealed three main spots (R_F = 0.08, 0.22, 0.44), one of which (R_F = 0.22) was evidently due to the unchanged depside. The remaining spots (R_F = 0.08 and 0.44) were indistinguishable from the spots of 1-*O*-methyl-orcinol-2,4-dicarboxylic acid and 2-methyl-6-hydroxy-orcinol-4-carboxylic acid, as established by co-chromatography with authentic samples. Thus the depside, with reasonable certainity, must be identified as hypothamnolic acid.

Squamatic acid and baeomycesic acid. S.moorei and *S. verrucigera* were treated as follows: The dry lichen (0.15–0.20 g) was extracted with acetone (3 × 5 ml) at 50° for 1 h. Upon concentration of the combined acetonic extracts, a crystalline precipitate was obtained, which was repeatedly recrystallised from glacial acetic acid, yielding a substance (1–2 mg), m.p. 223–225° (decomp.), identical with squamatic acid (mixed m.p., IR).

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

Dry *S. torulosa* (0.03 g) was extracted with acetone (2 × 0.5 ml) as above. Thin layer chromatography revealed two main spots (R_F = 0.28 and 0.50), in all respects identical with co-chromatographed squamatic acid and baeomycesic acid, respectively.

Thamnolic acid and decarboxythamnolic acid. Dry *S. decumbens* (0.3 g) was extracted with acetone (3 × 10 ml) at 50° for 1 h. Concentration of the combined acetonic 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 acetonic mother liquor revealed a spot (R_F = 0.50), in all respects identical with co-chromatographed decarboxythamnolic acid.

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1. Bruun, T. *Tetrahedron Letters* **1960** (4) 1.
2. Lindberg, B. and Meier, H. *Acta Chem. Scand.* **16** (1962) 543.
3. Mathey, A. *Private communication.*
4. Asahina, Y. and Nuno, M. *J. Japan. Botany* **39** (1964) 313.
5. Asahina, Y., Aoki, M. and Fuzikawa, F. *Ber.* **74** (1941) 824.
6. Shibata, S. In Linskens, H. F. *Modern Methods of Plant Analysis*, Vol. VI, Berlin 1963.
7. Stahl, E. *Dünnschicht-Chromatographie*, Berlin 1962.
8. Ramaut, J. L. *Bull. Soc. Chim. Belges* **72** (1963) 97.
9. Wachtmeister, C. A. *Acta Chem. Scand.* **9** (1955) 1395.
10. Asahina, Y. and Shibata, S. *Chemistry of Lichen Substances*, Tokyo 1954.
11. Asahina, Y. and Hiraiwa, M. *Ber.* **72** (1939) 1403.
12. Asahina, Y. and Ihara, S. *Ber.* **62** (1929) 1196.

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