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**BRITISH  
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*Nephroma*

*Peltigera*

chemistry



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A CHEMICAL CHECKLIST OF BRITISH LICHENS: Part 2.

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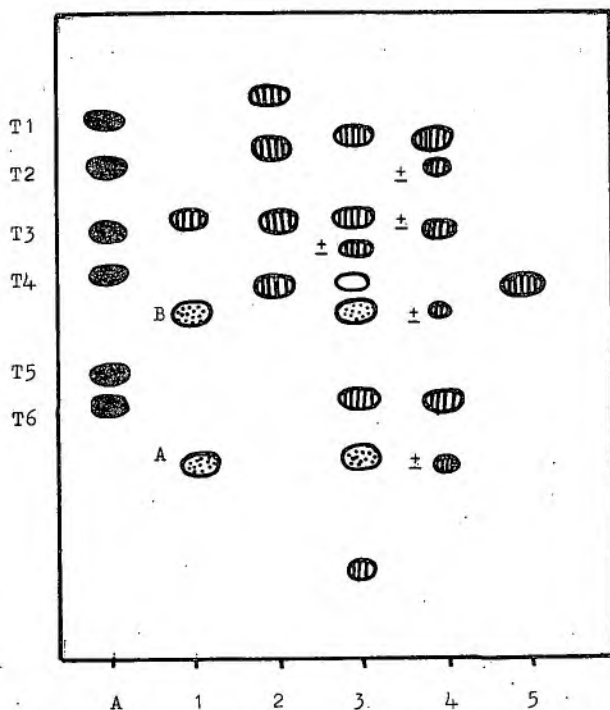
Introduction

The first part of this series (Parmelia) was published in Bulletin 58 following our 'Guide to Microchemical Techniques', published in Bulletin 57 (suppl.), which should be consulted for thin-layer chromatography (TLC) methods used.

The genera Nephroma and Peltigera have very similar chemistries, sharing a series of six major hopane triterpenoids (T1 to T6 below), whilst species of both genera with strongly tomentose upper surfaces lack lichen substances. The results of our chemical studies on Nephroma, as presented here, come from a detailed study of the genus which will shortly be published in The Lichenologist 19(3); this information is included for completeness since misidentifications between the species of the two genera are not infrequent. and may more readily be corrected if TLC analysis is undertaken.

A complete account of the chemistry of British Peltigera species has not previously been published. An example, describing the P. polydactyla species group, was illustrated by us in Bulletin 57 (suppl.):Fig.2. Similarly, Tønsberg and Holtan-Hartwig (Nord.J.Bot. 3: 681-688 (1983)) illustrated the various races occurring in the P. apthosa group. The latter work introduced the new solvent system EHF (diethyl ether : hexane : formic acid; 300:100:3) for separating hopane triterpenoids and related substances. This system was not used by us since we thought it would be more useful to provide characteristics of diagnostic substances, listed in descending order, in solvent system G, a more stable and reliable solvent system. EH or "HEF" (White & James 1985, 1986) together with standard systems (TA, TDA, HEF) should be used for more critical analyses since some substances may have similar Rf values and be masked or misinterpreted if run in G alone. Further, two-dimensional TLC is required to detect traces of substances related to tenuiorin that often occur in Peltigera (e.g. methyl evernate, methyl lecanorate,

TLC patterns of unidentified terpenoids in selected British  
Peltigera species in solvent EH.



Legend: A is a control of hopane triterpenoids T1-T6 (=solid circles). 1. P. britannica, 2. P. leucophlebia, 3. P. venosa, 4. P. scabrosa, 5. P. malacea. open circles= uvc+blue unknown, circles + vertical lines = unidentified terpenoids, circles + stippling = phlebic acids A & B.

and evernic, gyrophoric and lecanoric acids. Acetone extracts should, in all instances, be heavily loaded onto the TLC plates using a hot plate to concentrate the spots.

The Peltigera results presented here are based on those contained in an unpublished project by Mrs. R. Roberts (née Tucker), whilst an undergraduate at London University, together with analysis of recent additions to the British Flora and taxonomic and nomenclatural changes. Since the publication of a key to the British species by Vitikainen (Bulletin 50) Peltigera britannica has been recognised (Tónsberg and Holtan-Hartwig loc. cit.) as a distinct species from P. aphthosa. Material from the British Isles, previously called P. aphthosa, belongs to P. britannica and it seems likely that P. aphthosa sens. str. does not occur in the British Isles. P. britannica differs chemically from P. leucophlebia and may further be distinguished by the indistinct venation on the lower surface and peltate, button-like, easily removable cephalodia on the upper surface.

#### LEGEND

underlining indicates predominating substances

+ before substance = sometimes present, sometimes absent

+ to +++ after substance indicates quantity of substance (arbitrary by visual definition only)

(+) or (++) variability of amount from specimen to specimen

tr+ trace to small quantity of substance

uv+ a positive UV fluorescence before charring

uvc+ a positive UV fluorescence after charring

a = acid

p = purple

q = quenching (under UV light)

Hopane triterpenoids

T1	7 $\beta$ -acetoxyhopan-22-ol
T2	15 $\alpha$ -acetoxyhopan-22-ol
T3	hopane-6 $\alpha$ ,22-diol (zeorin)
T4	hopane-7 $\beta$ ,22-diol
T5	hopane-15 $\alpha$ ,22-diol
T6	hopane-6 $\alpha$ ,7 $\beta$ ,22-triol

NEPHROMA

- arcticum nephroarctin +(+) , usnic a tr, phenarctin +++ (overlying usnic acid in G), T3 +++,  $\pm$  methyl gyrophorate (rare). Best separation in "HEF" or a two way assay of this solvent with solvent G.
- helveticum unknown straw uv+q uvc+ vivid citrine accessory tr-,  $\pm$  T1, unknown dull blue-green (fading to beige) uv- uvc+ pink-brown accessory tr-, T4 +++. Apparently now extinct.
- laevigatum T6 +(++) , a complex series of anthraquinones (9 or more) uv+ orange-red +++(+) (rarely absent),  $\pm$  2 unknown mauve to colourless uv+ blue-grey uvc- accessories. Medulla K+p.
- parile T2+, unknown dull emerald green (beige on storage) uv+ uvc+ dull yellow-green accessory (+), T3 +++, T5 ++,  $\pm$  2 unknown mauve to colourless uv+ blue-grey uvc- accessories.
- resupinatum No lichen substances detected. Apparently now extinct (only known from 18th and 19th century collections from Aberdeenshire and Devon in the BM).
- tangeriense  $\pm$  T2, T3 +++,  $\pm$  T4, T6 +++, a complex series of anthraquinones (9 or more) uv+ orange-red +++(+). Medulla K+p.

PELTIGERA

aphthosa )  
britannica )

tenuiorin +++, methyl gyrophorate ++, unidentified terpenoid ++ (occupying same Rf as T2 in G, separating from T2 in EH), ± gyrophoric a tr, phlebic acids A & B ++ (uvc +++ deep olive-green, then rapidly uvc ++ purple-brown; appearing as a single spot in G, separating in EH).

canina

No lichen substances detected.

collina

tenuiorin +++, methyl gyrophorate +(++), ± T1 tr+, ± gyrophoric a tr, T3 +++, ± T6 tr, ± up to 4 unidentified terpenoids tr.

degenii

No lichen substances detected.

didactyla

No lichen substances detected.

elizabethae

tenuiorin +++, methyl gyrophorate ++, ± unidentified terpenoid tr-, ± T2 tr, ± gyrophoric a tr, T3 ++, ± T4 tr, ± traces of 2 or more unidentified terpenoids, unidentified terpenoid (Rf 1) tr-+ (as in P. horizontalis).

horizontalis

tenuiorin +++, methyl gyrophorate ++, ± gyrophoric a tr, T3 ++, ± T4 tr+, unidentified terpenoid (Rf 1) tr-+ (resolved into 3 spots above tenuiorin in EH).

lactucifolia

tenuiorin +++, methyl gyrophorate ++, T1 ++, T2 ++, ± gyrophoric a tr, T3 tr-, ± T4 tr.

lepidophora

No lichen substances detected.

leucophlebia

tenuiorin +++, methyl gyrophorate ++, unidentified terpenoid tr-, unidentified terpenoid ++ (as in P. britannica), ± gyrophoric a tr, unidentified terpenoid uvc ++ deep pink +++ (between T4 & T5 and slightly lower than phlebic acids A & B in G).

malacea

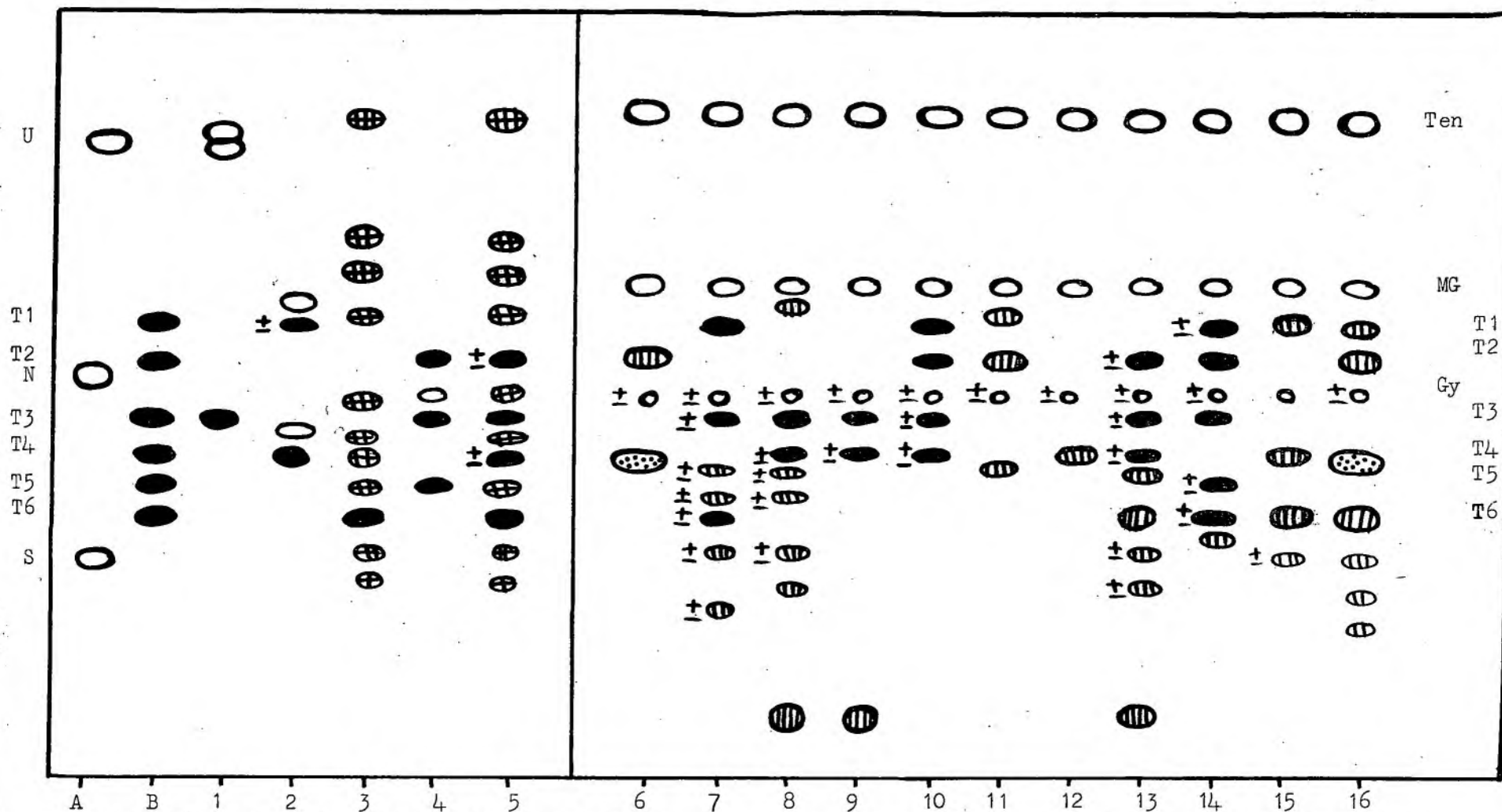
tenuiorin +++, methyl gyrophorate ++, ± gyrophoric a tr, unidentified terpenoid +++ (same as in P. leucophlebia; Rf as T4 in G but below in EH). Only Scandinavian material examined.

<u>neckeri</u>	<u>tenuiorin</u> +++, methyl gyrophorate tr-, <u>T2</u> +(+), + <u>gyrophoric a tr</u> , <u>T3</u> +( +), <u>T4</u> +( +), <u>unidentified</u> <u>terpenoid</u> +( +) (between <u>T4</u> & <u>T5</u> in G), <u>unidentified</u> <u>terpenoid</u> +( +) (same Rf as <u>T6</u> in G) [both these terpenoids were misidentified as <u>T5</u> & <u>T6</u> in White & James 1985], 2 unidentified terpenoids (Rf 2-3), + unidentified terpenoid (Rf 1) tr-+ (as in <u>P. horizontalis</u> ).
<u>polydactyla</u>	<u>tenuiorin</u> +++, <u>methyl gyrophorate</u> +( + +), + <u>T1</u> tr- + +, <u>T2</u> + + +, + <u>gyrophoric a tr</u> , <u>T3</u> ++(+), + <u>T5</u> tr, + <u>T6</u> tr, + <u>unidentified terpenoid</u> (brlow <u>T6</u> in G). Superficially similar to <u>P. lactucifolia</u> .
<u>praetextata</u>	No lichen substances.
<u>rufescens</u>	No lichen substances.
<u>scabrosa</u>	<u>tenuiorin</u> + + +, <u>methyl gyrophorate</u> ++, <u>unidentified</u> <u>terpenoid</u> ++ (as in <u>P. venosa</u> ), <u>gyrophoric a</u> +, <u>unidentified terpenoid</u> + (Rf same as <u>T6</u> , as in <u>P. venosa</u> ), + traces of unidentified terpenoids. Only Scandinavian material available for study.
<u>venosa</u>	<u>tenuiorin</u> + + +, <u>methyl gyrophorate</u> ++, <u>unidentified</u> <u>terpenoid</u> + (as in <u>P. scabrosa</u> ), <u>unidentified terpenoid</u> ++ (as in <u>P. britannica</u> ) & unknown uvc + blue substance, + <u>gyrophoric a tr</u> , <u>phlebic acids A &amp; B</u> + + +, <u>unidentified</u> <u>terpenoid</u> ++ (as in <u>P. scabrosa</u> ), + 2 or 3 unidentified terpenoids tr. (the uvc + blue substance and phlebic acids A & B separate in EH).

#### REFERENCES

- White, F.J. & James, P.W. 1985. A new guide to microchemical techniques for the identification of lichen substances. Bull.Br.Lichen Soc. 57 (suppl.):1-41.
- White, F.J. & James, P.W. 1986. A chemical checklist of British Lichens: Part 1. Bull.Br.Lichen Soc. 58:40-48.

TLC patterns of British species of Nephroma and Peltigera in solvent G.



**Legend:** Ten = tenuiorin, MG = methyl gyrophorate, Gy = gyrophoric acid. A & B are controls: U=usnic a, S=salazinic a, N=norstictic a, T1 - T6 = hopane triterpenoids. 1.N.arcticum, 2.N.helveticum, 3.N.laevigatum, 4.N.parile, 5.N.tangeriense, 6.P.britannica, 7.P.collina, 8.P.elizabethae, 9.P.horizontalis, 10.P.lactucifolia, 11.P.leucophlebia, 12.P.malacea, 13.P.neckeri, 14.P.polydactyla, 15.P.scabrosa, 16.P.venosa. solid circles=T1-T6, open circles=depsides,depsidones, pigments, circles + vertical lines =unidentified terpenoids, circles + cross-hatching = anthraquinones, circles + stippling = phlebic acids.