

Mariko NUNO*: **On the isolation of chemical ingredients
of *Usnea bayleyi* (Stirt.) Zahlbr.**

布 万里子*: *Usnea bayleyi* (Stirt.) Zahlbr.
の化学成分の分離について

According to Asahina¹⁾ the principal chemical substance contained in *Usnea bayleyi* is "eumitrin". He did not isolate eumitrin itself, but discussed its presence by the microchemical method and its reaction towards C in alcohol. Under the kind guidance of Dr. Asahina, the systematic separation of chemical contents of *Usnea bayleyi* was carried out by the present writer as follows.

An amount of air dried lichen thalli of *Usnea bayleyi* collected in Japan was put in contact with cold benzene for about 30 minutes. The red coloured filtrated benzene solution was evaporated partially, laid aside for some time, and filtrated from segregated precipitation of the main part of usnic acid. This benzene filtrate was evaporated to dryness, treated with a small amount of alcohol to separate insoluble usnic acid, and filtered. This alcohol filtrate was evaporated to dryness, treated with ether, and filtered. The filtrated ether solution was mixed with petroleum benzine so much as yet any precipitation occurred and then the reddish substances were filtered off. The deep yellow filtrate was evaporated to dryness. This residue was dissolved in a moderate quantity of a mixture of benzene and ethylacetate (3:1), for the column partition chromatography.

The fractions gained by the column partition chromatography, contained chemical substances in the following order of succession: usnic acid, impurities including barbatic acid, eumitrin B, eumitrin B+A, eumitrin A, impurities including zeorine, and unknown reddish substances.

Finally, eumitrin A and B obtained from above fraction, were recrystallized from benzene mixed with alcohol respectively, for the further purification.

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1) Asahina, Journ. Jap. Bot. 42: 1-9, 1967.

Properties of eumitrin A and B are mentioned below.

Eumitrin A—yellow short prisms, m. p. 204–205°; Rf (T. L. C.)²⁾: 0.39; readily soluble in acetone and chloroform, moderately in benzene, and sparingly in ether and alcohol; gives with ferric chloride in alcohol a reddish violet colouration and with bleaching powder in alcohol a deep yellow colouration; dissolves in caustic alkali with a faint yellowish colour and in concd. H₂SO₄ with a deep yellow to orange colour.

Eumitrin B—light yellow rather long prisms, m. p. 201–202°; Rf (T. L. C.)²⁾: 0.49; readily soluble in acetone and chloroform, moderately in benzene, and sparingly in ether and alcohol; gives with ferric chloride in alcohol a violet colouration and with bleaching powder in alcohol a deep yellow colouration; dissolves in caustic alkali with a faint yellowish colour and in concd. H₂SO₄ with a deep yellow to orange colour.

The lichen thalli of *Usnea bayleyi*, which were extracted with cold benzene, contain a certain mixture of fatty acids and depsidones. By the treatment with cold ether, caperatic and protolichestic acids may be demonstrated and then by the treatment with boiled acetone norstictic acid accompanied with a minor quantity of salacinic acid is obtained.

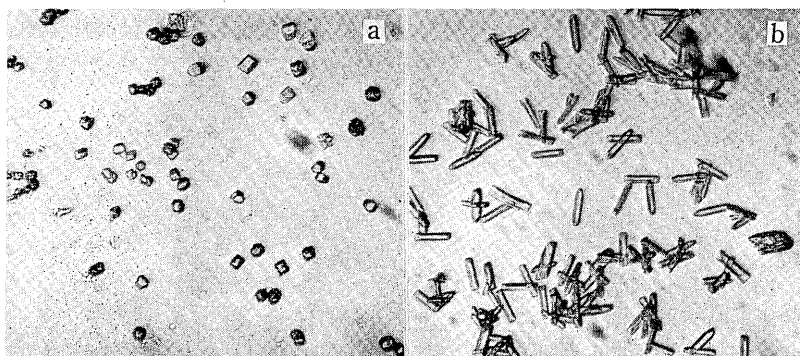


Fig. 1. Crystallization of a) eumitrin A (sensu Nuno) and b) eumitrin B (sensu Nuno) in G. E. solution.

- 2) Rf values for eumitrin A and B were demonstrated by thin-layer chromatography on Merck's Silicagel-G plates treated with 0.5 N-Oxalic acid. The chromatograms were developed in a benzene-ethyl-acetate-formic acid (5:2:0.1) solution and were detected as brownish spots by heating after having been sprayed with 10% H₂SO₄.

The further chemical investigation of eumitrins was entrusted to Dr. Shibata and his coworkers.

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本誌 42 卷 pp. 1-9 に於て朝比奈博士は *Usnea bayleyi* の重要な含有成分として eumitrin なる化合物を指摘された。その当時 eumitrin はスライドガラス上に共雑物（主にウスニン酸と色素）と同時に折出したものを顕微化学的にその形状で認定したもので (Fig. 1 参照), 其純品を捕えたのではなかった。そこで朝比奈博士の御指示に依り eumitrin を分離する為に本研究を行った。

その経路は、先づ日本産 *Usnea bayleyi* の赤色冷ベンゼン浸出液を少しく濃縮し、折出する粗ウスニン酸を除き、ベンゼン溶液を蒸発し、残留物を酒精で処理し、不溶のウスニン酸及び赤色物質を除去した母液を蒸発し、その残留物をエーテルで処理すると、若干の不純なウスニン酸が不溶解物として残る。これを母液に石油ベンゼンを加えてゆくと、赤色物質が綿屑様の沈澱となって折出・沈下する。この濃黄色を呈した母液を蒸発乾固し、その残留物をベンゼンに溶解したものをカラム用原液とし、蓆酸処理をしたシリカゲル管を通してカラムクロマト法による分離を行った。この時の溶媒はベンゾール：醋酸エチル=3:1 である。又、シリカゲルを蓆酸処理するには、0.5N-蓆酸溶液の中に 100 メッシュ前後のシリカゲルを一昼夜浸漬した後、母液を過圧搾し、蒸留水で洗滌脱水したものを更にアセトンで洗い風乾後、100-110° で 1 時間乾燥したものをを用いた。カラム法に依り溶出された成分は、不純物、ウスニン酸、バルバチン酸を含む不純物、eumitrin B, eumitrin B+A, eumitrin A, ゼオリン混入の不純物、赤色物質等の順にフラクションとして得られた。尚、以上の各フラクションの成分を確認するには T. L. C. 法に依った。

口児玉 務：近畿地方の苔類 (第 1 部), 大阪市立自然科学博物館発行, 116 頁。定価 800 円。著者の児玉務氏は関西の有力な苔類研究家で、過去 20 年以上にわたり近畿地方の苔類を調べられていた。その成果が、今回、大阪市立自然科学博物館収蔵資料目録第 3 集として発刊されることとなり、その第 1 部 (概説, コマチゴケ目, ウロコゴケ目の一部) が発行された。内容は苔類の分類のための手ほどきから、各目, 科, 属の重要な特徴が多数の図解と共に要領よくまとめられている。種類については図があるものもあるが、近畿地方での生態や分類学的ノートがあり、産地が上げてある。資料目録であるので致し方ないが、産地の極めて詳細な記録がつづく所があり、著者がいかにつまびらかに調査したかがうかがえる。藓苔類のガイドブックの少ない日本では、貴重な出版物といえる。問合せ先は大阪市西区観公園, 大阪市立自然科学博物館内, 大阪自然研究会。 (井上 浩)