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**The occurrence of porphyrilic acid in the genus
Stereocaulon and the identity of dendroidin^{****}**

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ポルフィリル酸のキゴケ属における産出および
デンドロイジンとの相同性について^{****}

In this note we wish to report the isolation of dendroidin from several species of the genus *Stereocaulon* and to show that it is identical with porphyrilic acid in all of the cases we have so far studied.

In 1961 the eminent lichenologist Asahina reported the occurrence of a "diphenylene oxide derivative" which he called dendroidin in four species of *Stereocaulon*¹⁾. The substance was found to have a m. p. of 293°, to give a bluish-green color with alcoholic ferric chloride and a dark bluish-green with aqueous calcium hypochlorite. A molecular formula of C₁₆H₁₂O₈ was suggested.

Porphyrilic acid is a dibenzofuran derivative which is supposed to have the structure I shown in fig. 1. This structure is not entirely proved to our satisfaction since the alternative structures II and III in fig. 1 are also possible (Wachtmeister, 1956)²⁾. Porphyrilic acid has been isolated from the crustose lichen *Haematomma coccineum* (Dicks.) but has not to our knowledge been found in other lichen genera.

In the course of a chromatographic investigation of the genus *Stereocaulon* (I. M. Lamb and C. Fox, in preparation) there was repeated occurrence of a spot that remained near the origin in most solvents, gave a blue-green

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**** This paper is dedicated to Prof. Yasuhiko Asahina in recognition of his many contributions and his longstanding interest in the genus *Stereocaulon*.

1) Journ. Jap. Bot. 36: 65. 1961.

2) Acta Chem. Scand. 10: 1494. 1956.

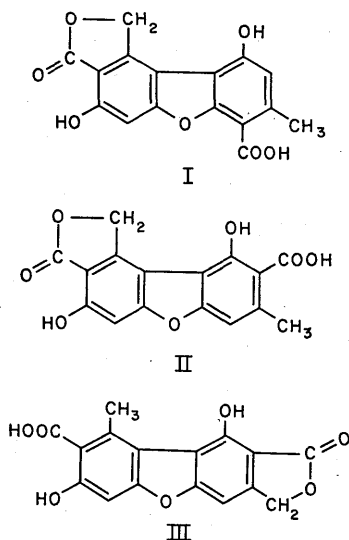


Fig. 1. Chemical structures of porphyrilic acid.

coloration with ferric chloride and a blue-green one when sprayed with aqueous hypochlorite solution. The substance was chromatographed with an authentic sample of dendroidin generously provided by Prof. Asahina.

The only samples of material then available for immediate investigation consisted of a small amount of *S. pendulum*. This was extracted and purified to yield 14.4 mg of virtually pure dendroidin. High resolution mass spectrometry indicated an empirical formula of $C_{16}H_{10}O_7$ and this finding, along with identical color reactions and melting point, indicated that porphyrilic acid and dendroidin are the same. Unfortunately the

sample contained a small amount of an unknown contaminant that could not be removed by recrystallization, and confirmation could only be made by the formation of the decarboxylation product, porphyrilin.

A somewhat larger sample became available from a collection of *S. botryosum* Ach. emend. Frey. This material can be definitely stated to contain porphyrilic acid on the basis of identical NMR, IR, UV, mass spectra, and by the formation of a decarboxylation product, porphyrilin.

A third sample consisted of bulk *S. explanatum* I. M. Lamb and it was also found to contain porphyrilic acid. In addition, chromatographic evidence in six solvent systems has been obtained. This shows porphyrilic acid occurs in at least 10 other species of the genus. Unfortunately, most of these species occur in such remote and exotic places that it will be impossible to obtain satisfactory chemical confirmation for each case.

Approximately 400 specimens representing members of each of the species of the genus *Stereocaulon* have been examined to date. The occurrence of porphyrilic acid has been found constant in seven species of the genus. In three others, the occurrence is inconstant and may be considered to be an

example of chemical variation. The taxa now considered to constantly contain porphyrilic acid are: *St. pendulum* Asah., *St. dendroides* Asah., *St. strictum* Th. Fr., *St. explanatum* M. Lamb, *St. botryosum* Ach. emend. Frey., *St. leprocephalum* Vain. and an arctic species as yet unnamed belonging to the *St. vesuvianum* assemblage. Those in which the occurrence is not constant are *St. piluliferum* Th. Fr. and *St. pomiferum* Duvign. and a Himalayan species as yet unnamed belonging to the *St. massartianum* assemblage. An extensive treatment of the taxonomy and locations will appear at a later date.

The biogenetic significance of dibenzofurans has recently been reviewed by Mosbach (1969)³⁾. Porphyrilic acid is of interest in that the compound probably is derived from the oxidation of two orsellinic acid units resulting in decarboxylation, phenolic and ethereal coupling, and the formation of the lactone ring, not necessarily in that order. It is, to our knowledge, the only orsellinic acid-derived compound that occurs in the genus *Stereocaulon* and for this reason, may be of some taxonomic aid to botanists working with this difficult genus.

Experimental

Isolation of Dendroidin from *S. pendulum*. The air dried lichen (5.5 g) was extracted with two changes of anhydrous ether (1 liter each). This ether extract was in turn extracted with three portions of cold 5% NaHCO₃, followed by extraction with three portions of 5% Na₂CO₃. The aqueous extracts were immediately acidified with HCl and the resulting precipitates were collected by filtration after standing in a cold room overnight.

The bicarbonate fraction was found to contain all of the dendroidin detectable on thin layer chromatograms. This was washed with a small amount of cold acetone and the insoluble portion was recrystallized from acetone and subsequently from dioxane. In other preparations, it was found that the solvent of choice for crystallization of porphyrilic acid is methyl ethyl ketone.

The melting point determination of this substance is so characteristic that it is virtually diagnostic. The substance melts with gaseous decomposition at 283° (uncor.). A white ring of sublimed material gathers above the melt and if the temperature was held at the melting point white needles

3) Mosbach, K. *Angewandte Chemie*, 8: 240. 1969.

were extruded from the melt. When the temperature was raised to 293–296° the needles melted to form a reddish-black residue. Mixed melting points of material from *Stereocaulon* species with authentic porphyrilic acid in all cases gave identical results.

Infra-red spectra of authentic porphyrilic acid and of the material from the lichen sources show peaks at 3410, 3220, 1711, 1680, 1589, 1463, 1432, 1412, 1261, 1215, 1132, 1088, and 1060 cm^{-1} (KBr). The UV spectrum showed peaks at 327, 285, and 247 nm.

The di-trimethylsilyl ether mono-trimethylsilyl ester of both known porphyrilic acid and that from *S. botryosum* were prepared by the method of Waiss, Lundin, and Stern (1964)⁴. The NMR spectra of these derivatives were determined in carbon tetrachloride with TMS as internal standard. The spectra of the two samples were found to be identical. Two sharp singlets at 3.17 and 3.47 τ represent two aromatic protons. A sharp singlet at 4.62 τ and another at 7.28 τ represented two methylene and three methyl protons respectively.

Final proof of the relationship between dendroidin and porphyrilic acid was provided by the degradation of dendroidin to porphyrilin. Ten milligrams of both substances were dissolved in acetone and a thin layer of the material was distributed over the bottom of a sublimation tube. The sublimator was closed and evacuated to about 2 mm Hg. The sublimator was heated in a bath of silicone oil. When a temperature of 230° was reached a rapid deposition of material on the cold finger began and after slowly raising the temperature to 285° over 10 minutes, the apparatus was cooled and opened. The decomposition of both porphyrilic acid and dendroidin was nearly quantitative, yielding a faintly yellowish microcrystalline powder. Two recrystallizations from an acetone-ether mixture in both cases yielded pure porphyrilin (m. p. 295–300° subl.). The loss of a carboxyl group was confirmed by disappearance of bands at 1711 and 1680 cm^{-1} and by mass spectra.

Chromatographic Analysis of Herbarium Specimens. Approximately 100 mg or less of lichen material was removed from herbarium packets and placed in polyethylene capsules. (Beem capsules used for embedding electron micro-

4) Tetrahedron Letters. 1964: 513. 1964.

scope specimens). The lichen material was crushed with a blunt stylus and enough acetone was added to completely cover the specimen. The acetone was allowed to evaporate to half its volume and samples were withdrawn with very fine capillary pipettes ($\sim .5$ mm). The samples were spotted on half sheets of Eastman Chromatogram Sheet 6060. The sheets were developed from the shorter direction so that the solvent travelled about 90 mm. These short chromatograms were necessary because of the large numbers of chromatograms and the small amounts of material available from the herbarium packets. Each specimen was chromatographed at least once in six solvent systems. These were: 1. Benzene—dioxane—acetic acid 90 : 25 : 4; 2. Benzene—methanol—acetic acid 95 : 10 : 5; 3. Toluene—methylene chloride—acetic acid 10 : 30 : 1; 4. Toluene saturated with formic acid; 5. n-Hexane—ethyl acetate—formic acid 100 : 25 : 1 and 6. Butanol—acetone—water 5 : 1 : 2. Spray reagents consisted of the following: 1% aqueous ferric chloride; diazotized benzidine (10% aqueous NaNO_2 mixed with equal amounts of 1.5% benzidine in 7% HCl); Fast Bordeaux (0.1% in water) followed by over spray of saturated sodium carbonate; and p-nitrobenzenediazonium fluoroborate in acetone followed by 2M sodium carbonate solution. All of the samples reported here were chromatographed at least nine times and in some cases 12 or more. Each chromatogram was accompanied by a reference mixture containing an extract of *S. pendulum*.

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朝比奈先生は1961年にある種のキゴケ属地衣がデンドロイジンを産することを報告された。一方, Wachtmeister (1956) は固着地衣 *Haematomma coccineum* からポルフィリル酸を得, その化学構造は fig. 1 に示した II または III であるとした。著者等はシダレキゴケ *Stereocaulon pendulum* からデンドロイジンを抽出し, それがマスペクトル, 呈色反応, 融点などでポルフィリル酸と一致すること, および, 脱炭酸によってポルフィリリンが得られるので, 両者が同一物質であることを認めた。シダレキゴケの材料を多量に入手することが困難であるため, *St. botryosum* から得た物質 (デンドロイジン) についても NMR, IR, 紫外線分析, マスペクトルなどを行ない, 両物質が相同であることを確認した。なお, ポルフィリル酸は *Stereocaulon pendulum*, *St. dendroides*, *St. strictum*, *St. explanatum*, *St. botryosum*, *St.*

leprocephalum, および *St. vesuvianum* 群の 1 種では常成分として出現し, *St. piluliferum*, *St. pomiferum*, および *St. massartianum* 群の 1 種では非常成分として出現する。

○学名改訂 2 件 (山崎 敬) Takasi YAMAZAKI: New combination and new name in two taxa

1) 小笠原学術調査の一部として, 植物目録を作るにあたり, 下記のものは自動的に学名の変更を必要とする。

Symplocos pergracilis (Nakai) Yamazaki comb. nov.

Bobua pergracilis Nakai in Bot. Mag. Tokyo 44: 24 (1930)—*Dicalix pergracilis* (Nakai) Hara, Enum. Sperm. Jap. 1: 106 (1948)—チチジマクロキ
Distr. Isls. Bonin, Isl. Chichizima.

ハイノキ属は外観は皆よく似ているが, おしべの形や子房の構造にかなり変化があり, Brand (1901) は 4 亜属に分類した。中井猛之進氏 (1927) はいくつかの属にわけるべきであるとして, 日本のものをハイノキ属 *Bobua* とサワフタギ属 *Palura* とにわけた。初島住彦氏 (1936) はミヤマシロバイ属 *Cordyloblaste* を追加している。しかし現在でも *Symplocos* 一属としてあつかう人が多く, 属をわけてもその境はかならずしも明瞭でないようである。同一属内の変異としてあつかう方が適当と思う。

2) 本誌 44: 317 で *Salvia formosana* という新組合せを作ったが, すでに早田文蔵氏が台湾のキバナアキギリに同名を使っていることを, 原寛氏が指摘された。調査不十分で余計な名を作ったことをおわびすると共に, 新名を作ることにする。

Salvia muratae Yamazaki nom. nov.—*Salvia formosana* (Murata) Yamazaki in Journ. Jap. Bot. 44: 319 (1969) non Hayata 1919.

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□内藤蕉園著・難波恒雄解説: 詳解古方薬品考 原著は江戸時代末の医家内藤尚賢の作で, 220 余種の薬物の薬性, 功用を述べ, 当時の京都の著名な画家を動員して画かせた詳細な挿図を伴っている。大部分が植物で, この図によって江戸時代に日本で使っていた薬用植物が, どのようなものであったかが明瞭にわかる貴重な本である。また長年にわたって東亜の薬用植物の研究をしている解説者の詳細な説明があり, 書中の薬物の中国での原植物, 日本でそれにあてて使用した植物, その使用法など, 最近の研究結果がくわしくのせられていて, 単なる解説以上のくわしい説明があり, 薬用植物の研究にとって貴重な解説である。A5 判, 760 頁, 6,000 円。昭和 44 年 10 月刊。東京都新宿区納戸町 45 大山茂方, 古方薬品考刊行会。

(山崎 敬)