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1′-CHLOROPANNARIN, A NEW DEPSIDONE FROM *ARGOPSIS FRIESIANA*: NOTES ON THE STRUCTURE OF PANNARIN AND ON THE CHEMISTRY OF THE LICHEN GENUS *ARGOPSIS**

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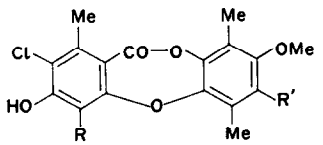
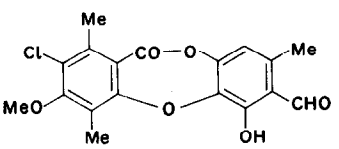
Abstract—A new depsidone 1′-chloropannarin has been isolated from the lichen *Argopsis friesiana* Müll. Arg. and synthesized by chlorination of pannarin. A revised structure of pannarin, and notes on the chemical constitution of *Argopsis friesiana* Mill. Arg. and *A. megalospora* Th. Fr., are given.

INTRODUCTION

The lichen genus *Argopsis* (family Stereocaulaceae) comprises two species, *A. megalospora* Th. Fr. (subantarctic islands of New Zealand) and *A. friesiana* Müll. Arg. (Kerguelen and Crozet Islands). A taxonomic revision of these species has been published by Lamb [1]. A third species described by Lamb, *loc. cit.*, and doubtfully assigned to the genus, *Argopsis* (?) *cymosoides* Lamb, is now taxonomically reassigned as a form of *A. friesiana*. The genus *Argopsis* resembles *Stereocaulon* in morphology, being fruticulose with assimilative phyllocladia containing Chlorophycean algae and cephalodia containing Cyanophycean algae, but differs in having muriform or submuriform spores (in *Stereocaulon* the spores are transversely septate).



	R	R′
(1)	CHO	Cl
(2)	CHO	H
(4)	Me	Cl



(3)

Bodo and Molho [2] recently reported on the isolation and structure of a new chlorodepsidone *argopsin* (**1**) from *A. friesiana* (erroneously called by them *A. megalospora*). We have independently

* Part 106 in the series "Lichen Substances". Part 105: Follmann, G. and Huneck, S. (1974) *Philippia* **2**, 129.

investigated both *Argopsis* species and found that *A. megalospora* contains atranorin, fumarprotocetraric acid, psoromic acid, and perlatolic acid in varying proportions, while *A. friesiana* contains atranorin and argopsin (the latter constituent of inconstant occurrence), and we here report on the structure and identity of argopsin with 1′-chloropannarin (**1**).

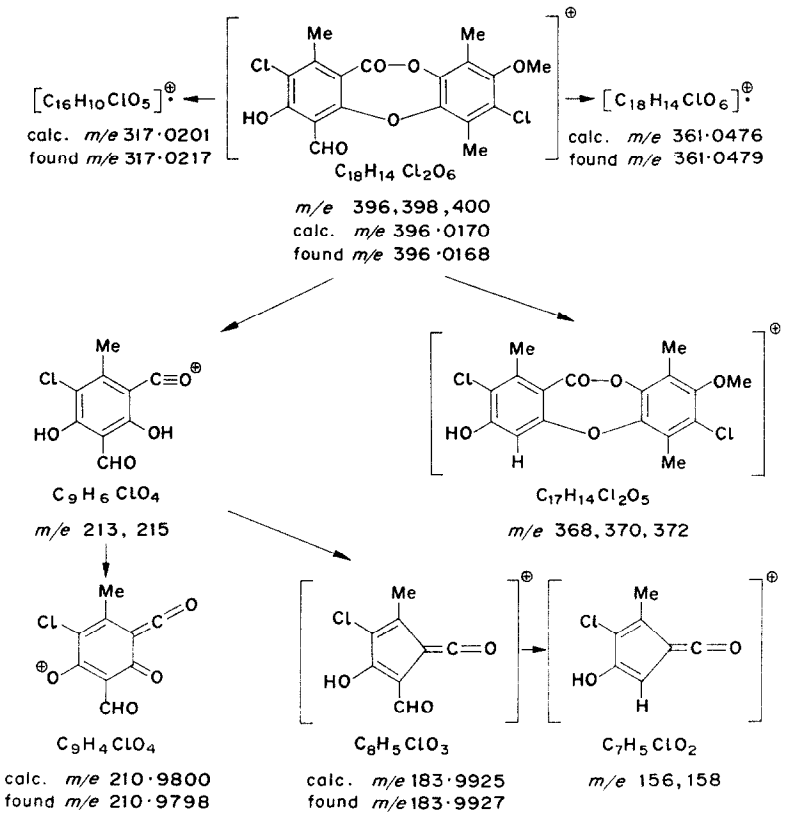
RESULTS AND DISCUSSION

After the separation of atranorin by means of preparative TLC on silica gel and crystallization we obtained **1** as faint yellowish prisms which showed a positive Beilstein test and were colored red with $FeCl_3$ (in EtOH) and orange with *p*-phenylenediamine (in EtOH). The MS of (**1**) gave in the region of the molecular ion three peaks at *m/e* 396, 398, and 400 in the ratio 9:6:1, corresponding to a content of 2 atoms of chlorine in the molecule; the high resolution measurement gave the formula $C_{18}H_{14}Cl_2O_6$ (calc 396·0170; found 396·0168). The UV spectrum of (**1**) was typical for depsidones and was almost identical with that of pannarin (**2**).

In the IR spectrum an aldehyde band at 1725 cm^{-1} and a hydroxyl band at 3500 cm^{-1} were observed. The NMR spectrum of (**1**) was also very similar to that of pannarin (Table 1) and showed the presence of three aromatic methyl groups, one methoxyl group, one aromatic aldehyde group and one phenolic hydroxyl group.

Finally, we were able to prove the presumed identity of the depsidone isolated from *A. friesiana* with 1′-chloropannarin by partial synthesis. Pannarin, on treatment with chlorine in acetic acid, furnished a compound which was identical with the natural product in all respects. For the fragmentation of chloropannarin on electron impact see Scheme 1.

Yosioka [3] suggested structure (**3**) for pannarin on the basis of degradation experiments, but this structure, from biogenetic considerations, is improbable, and was corrected by Sargent [4] to structure (**2**). Since Bodo and Molho [2] have



Scheme 1. Fragmentation of 1′-chloropannarin (1) on electron impact.

Table 1. NMR spectra of 1'-chloropannarin (**1**) and pannarin (**2**)

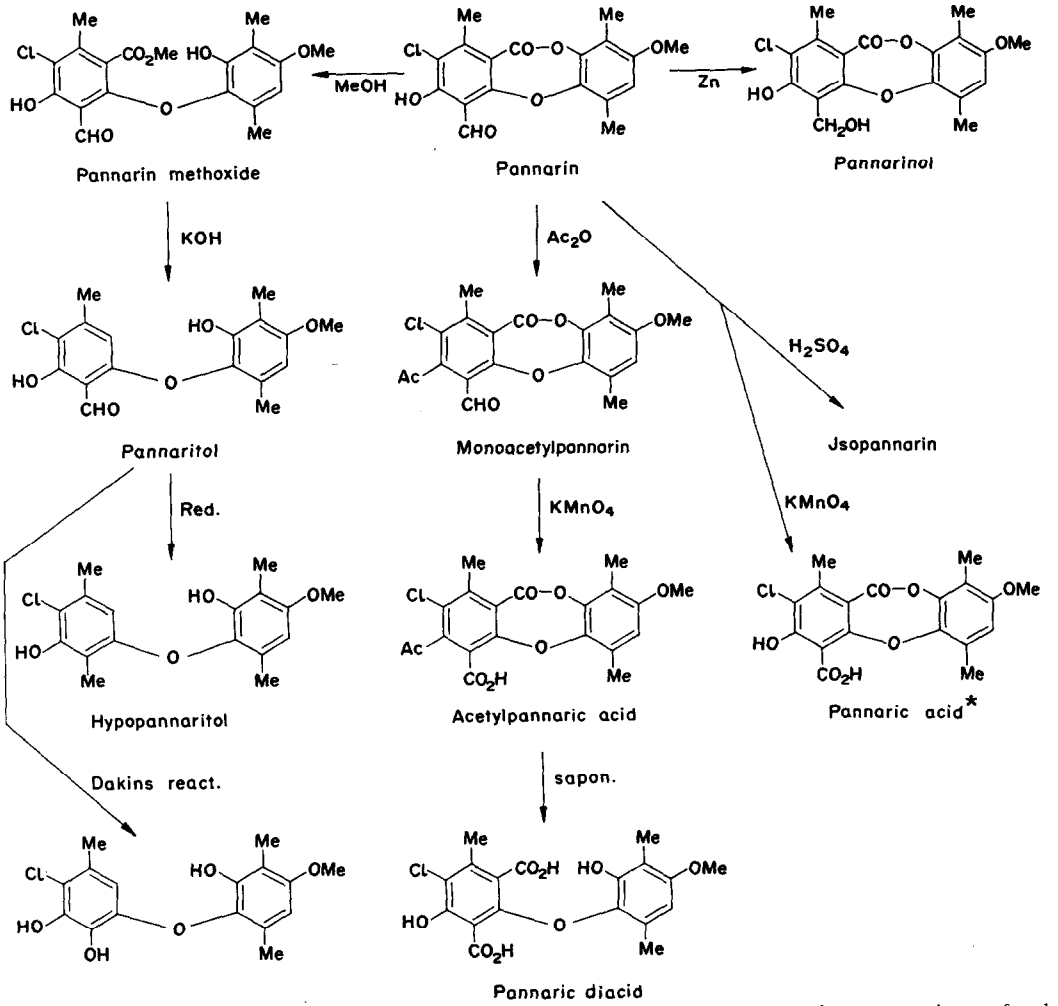
	Group	6'-Me	-Me	-Me	-OMe	-CHO	-OH	-H
1	60 MHz	2·32	2·46	2·58	3·81	10·62	12·66	
	100 MHz	2·34	2·47	2·62	3·82	10·70	12·80	
2	60 MHz	2·25	2·41	2·61	3·85	10·72	12·85	6·44

All δ values in ppm.

correlated argopsin (= 1'-chloropannarin) with vicanicin (**4**) by Clemmensen reduction, and the structure of vicanicin was determined by X-ray analysis [5], the transformation of pannarin into argopsin affords a further proof for structure (**2**) for pannarin. As a result of the new structure of pannarin, the degradation scheme of Asahina and Shibata [6] must be altered as shown in Scheme 2.

EXPERIMENTAL

Isolation of 1'-chloropannarin (**1**) *from* Argopsis friesiana. Air-dried and ground lichen (10·0 g, collected in 1960 in the Crozet Islands, southern Indian Ocean, by H. W. Tilman and determined by I. M. Lamb, Monogr. no. 5991) was extracted with Et_2O (2 × 8 hr) to yield 0·12 g of a mixture of 1'-chloropannarin (**1**) and atranorin. The mixture was dissolved in 4 ml $CHCl_3$ and applied to a 40 × 40 cm TLC plate coated with Si gel PF 254–366 (Merck) of 1 mm thickness. After development with cyclohexane–$CHCl_3$–methylethylketone (9:4·5:0·5), the lower band (located under UV



Scheme 2. Revised scheme for the degradation of pannarin (2). * This compound must not be confused with the dibenzofurane "pannaric acid".

light) was extracted with MeOH–Et_2O and the residue after evaporation of the solvent was recrystallized 2× from CH_2Cl_2–MeOH to give 10·5 mg (0·1%) of 1′-chloropannarin (**1**) as faint yellowish prisms, mp 205–207° and R_f 0·43 (Kodak Chromaplate 6061, cyclohexane–$CHCl_3$–methylethylketone (9:4·5:0·5), giving an orange spot after spraying with an EtOH soln of *p*-phenylenediamine. UV; λ_{max}^{MeOH} nm (log ϵ): 213 (4·24), 250*s* (4·04), 310 (3·57), 360 (3·30). UV spectrum of pannarin (**2**), λ_{max}^{MeOH} nm (log ϵ): 212 (4·21), 234 (4·14) 250*s* (4·04), 310 (3·47), 350 (3·30). TLC also indicated the presence of a small amount of atranorin. The upper band of the preparative TLC separation furnished 11 mg (0·1%) of atranorin mp 194–196°.

Chlorination of pannarin. To a soln of 21 mg pannarin (**2**) in 5 ml of AcOH was added a soln of 0·6 mg Cl_2 in 0·5 ml AcOH, and the mixture kept for 24 hr in the dark at room temp. After diln with H_2O the ppt. was filtered, washed with H_2O, dried at room temp. and recrystallized 2× from CH_2Cl_2–MeOH to yield 10 mg of faint yellowish prisms, mp 207–208°, identical by mmp, IR, UV, NMR and MS with 1′-chloropannarin isolated from *A. friesiana*. IR (in KBr): 698, 732, 762, 808, 878, 900, 1008, 1030, 1042, 1090, 1116, 1160, 1218, 1256, 1300, 1356, 1410, 1450, 1464, 1562, 1640, 1725, 2960, and 3500 cm^{-1}.

Chemical constitution of specimens of Argopsis friesiana *examined.* Further study of material from Kerguelen made available after the taxonomic revision of Lamb [1] was completed indicates that *Argopsis* (?) *cymosoides* Lamb (*op. cit.* p. 455) is conspecific with *A. friesiana*, and accordingly it is now nomenclaturally recombined as *Argopsis friesiana* f. *cymosoides* (Lamb) Lamb, n. comb. (direct basionym reference: *Argopsis* (?) *cymosoides* Lamb [7]), a form differing from the typical species in dwarfer growth, compact pulvinate habitus with corymbose branching and small subcoralloid phyllocladia densely concentrated on the upper surface of the tufts, giving the plants an aspect very similar to *Stereocaulon cymosum* Cromb. *A. friesiana* may occur in a deficient phase containing atranorin only. The following specimens were examined by TLC: A. Typical species (f. *friesiana*). (a) Normal chemical spectrum with atranorin and 1′-chloropannarin (argopsin). Crozet Islands. Tilman, 1960 (BM, FH), fertile. (b) Deficient phase with atranorin only. Kerguelen. Tilman, 1960 (BM, FH), fertile; Imshaug, 1971, no. 49318 B pr. p. (FH, MSC), fertile. B. F. *cymosoides* (Lamb) Lamb. Normal chemical spectrum with atranorin and 1′-chloropannarin. Kerguelen. Aubert de la Rüe, 1949 (including the type specimen of f. *cymosoides*) (FH), sterile; Imshaug, 1971, no. 49318 B pr. p. (FH, MSC), sterile.

Chemical constitution of specimens of Argopsis megalospora *examined.* In the study of Lamb [1], two chemical strains of the species were distinguished, one (Strain I) with atranorin, fumarprotocetraric acid, occasionally also protocetraric acid, perlatolic acid, and sometimes one or two additional unidentified substances; the other (Strain II) with atranorin, psoromic acid, and sometimes one additional unidentified substance. Further chromatographic studies have since shown, however, that fumarprotocetraric and psoromic acids may occur together in the same specimen, for which reason the observed chemical variants of this species should be regarded as chemical phases, with fluctuating concentrations of constituents, rather than as strains. The following specimens were chromatographically examined:

Phase I, with atranorin, fumarprotocetraric acid, perlatolic acid, and psoromic acid. Campbell Island. Murray, 1959, no. 3677 (FH), fertile; Harris, 1969, no. 4926 (FH, MSC), fertile.

Phase II, with atranorin, fumarprotocetraric acid, psoromic acid, and an unidentified *p*-phenylenediamine-positive substance. Campbell Island. Rae, 1959, no. 4331 (FH), fertile.

Phase III, with atranorin, fumarprotocetraric acid, and perlatolic acid. Campbell Island. Filhol, 1874 (FH, PC), fertile; Harris, 1969, no. 4745 (FH, MSC), fertile; Imshaug, 1970, no. 46773 (FH, MSC), fertile. Auckland Islands. Easton, 1944 (FH), fertile.

Phase IV, with atranorin, psoromic acid, and an unidentified *p*-phenylenediamine-positive substance. Auckland Islands. Godley, 1963, no. 1266 (FH), fertile.

Voucher samples of the specimens of *A. friesiana* and *A megalospora* listed above are preserved in the herbaria mentioned: Department of Botany, British Museum (Natural History), London, England (BM); Farlow Herbarium, Harvard University, Cambridge, Massachusetts, U.S.A. (FH); Department of Botany, Michigan State University, East Lansing, Michigan, U.S.A. (MSC); and Laboratoire de Cryptogamie, Muséum National d'Histoire Naturelle, Paris, France (PC).

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