THE LICHENS IN BARIO HIGHLANDS: THEIR NATURAL OCCURRENCE AND SECONDARY ETABOLITES

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ABSTRACT

A total of 36 lichen **specimens** *from 13 genera was collected from the heath forest of Barb Highlands.* Thirty-five *specimens were identified to species level and one to generic level. Of the species identified, seven represented new records for the island of Borneo. One species,* Parmotrema acrotrychum was *previously known only from Papua New Guinea and Queensland, Australia and this study had significantly extended its distribution range to the western region. Three Asia-Australia species* Parmotrema subcoral linum, Physcidia cylindrophora *and* Relicina sublanea *were also discovered in this study*

INTRODUCTION

The wide diversity of lichen flora in Malaysia has encouraged many researchers to investigate their distribution, taxonomy, ecology, chemistry and the biological activity of their secondary metabolites. Reports on the distribution, chemotaxonomy and *in vitro* biological activities of lichens and their secondary metabolites have amply demonstrated their scientific importance and the utilitarian potential of Malaysian lichen flora (Din et al. 1992). A number of studies on the lichens of Sabah have also appeared in the literature of late. A total of 286 species of lichens has been documented from Mount Kinabalu (Sipman, 1993) and several chemotaxonomic studies of lichens from Sayap-Kinabalu Park (Samsudin et al. 1995a; 1995b) has also been carried out in recent years. To date, very few published reports on the lichens of Sarawak exist. Some of the earlier studies were recorded by Sammy (1980a, 1980b), Wolseley (1991) and Din et al. *(1995).* A bibliography of Malaysian lichenology has been published to provide a general perspective on the study of lichens in Malaysia (Galloway, 1994). in this paper we report our preliminary findings on the lichens collected from Bario Highlands, Sarawak as part of our continuing effort to study the lichens of Malaysia.

MATERIALS AND METHOD

The lichen specimens were collected from kerangas forest (30 4' 22" N, 1150 27' 53" E) and deposited in UNIMAS Herbarium. The lichen fragments were freed as far as possible of any trace organic substrate materials and secondary metabolites were extracted with warm acetone for thin-layer chromatography (TLC). Compounds were characterized by TLC using the methods standardized [or lichen products (Culberson, 1972; Culberson & Johnson, 1982; Elix & Ernst-Russel, 1993) and gradient-elution high performance liquid chromatography (HPLC) (Feige et al. 1993).

RESULTS AND DISCUSSION

Phytochemistry. The TLC and HPLC analysis on the 36 specimens showed that 33 contained secondary metabolites and three specimens, *Crocynia* sp. (Bario 2), *Dictyonema sericeum* (Bario 9) and *Parmeliella brisbanensis* (Bario 36) contained no compounds conventionally associated as lichen substances (Table 1).

The following classes of compounds were detected in the lichens examined: depsides, depsidones, dibenzofurans, triterpenes, fatty acids and pigments (including 4-ylidenetetronic acids, ergochromes, a quinone and an unknown).

The representatives of the genus *Pannotrema (P acrotrychum, P cristiferum, P cf cristiferum, P subarnoldii, P subcorallinum* and *P sulphuratum)* examined collectively contained the largest number of secondary metabolites including the depsides atranorin and chloroatranorin; the depsidones protocetratic acid, fumarprotocetraric acid, succinprotocetraric acid, salazinic acid and consalazinic acid; the fatty acids, lichesterinic acid, protolichesterinic acid and an unknown; and the intense yellow pigment (a 4-ylidenetetronic acid), vulpinic acid.

Of the individual species, *Pseudocyphellaria crocata* produced the largest number of lichen substances — the depsides tenuiorin and methyl gyrophorate; the depsidones stictic acid, constictic acid and cryptostictic acid; the triterpene, hopane-6u, 7~, 22-triol; and the 4-ylidenetetronic acid pigments, pulvic dilactone and calycin. Many of these substances or their biosequentially related derivatives were also detected in the various *Lobaria* species examined, namely *L. crassioi L. discoloi* L. *isidiophora and L. pseudopulmonaria.* Collectively these species contained the depsides gyrophoric acid and 4-O-methylgyrophoric acid; and depsidones stictic acid, constictic acid, cryptostictic acid, norstictic acid, salazinic acid and menegazziaic acid; an unknown triterpene and the pigment, thelephoric acid. These chemical parallels underline the close relationship between the genera *Lobaria* and *Pseudocyphellaria*, both members of the lichen family Lobariaceae.

Distribution. Of the lichen species identified, 7 represent new records for the island of Borneo including *Cladonia crispata* var. *cetrariiformis, Parmotrema acrotrychum, P subcorallinum, P sulphuratum, Physcidia cylindrophora, Relicina abstrusa* and *R. sublanea.* Previously *Parmotrcma acrotrychum* was known only from Papua New Guinea and Queensland (Australia). So the present new record marks a significant westerly extension of the range of this species.

Three of the above species have Asian-Australasian distributions, namely *Parmotrema suhcoral 1 mum, Physcidia cyl indrophora* and *Relicina sublanea*, while *Parrnotrema sulphuratum* and *Relicina abstrusa* are pantropical species. All five of these species are known from adjacent areas (e.g. Indonesia, Peninsular Malaysia, the Philippines, Papua New Guinea), indeed their occurrence in Sarawak is not unexpected. *Cladonia crispata* var. *cetrariiformis* on the other hand is a cosmopolitan species known from Europe and North America as well as from Indonesia, Papua New Guinea, Australia and New Zealand.

Table 1: Genus/Species and the Chemical Constituents of the Lichens

Specimen	**Genus/Species**	**Chemical Constituents**
Bario 44	*Cladonia crispata* var. *cetrariiformis* (Del.) Vain.	Squamatic acid
Bario 19 Bario 43	*Clad onia didyma* (Fee) Vain. var. *vulcania* (Zoll.& Moritze) Vain.	Thamnolic acid (minor), rhodocladonic acid (minor), didyrnic acid (major), condidyrnic acid (minor)
Bario 14 Bario 32	*Cladoniafruticulosa* Kremp.	Fumarprotocetraric acid
Bario 3	*Cladonia siamea* des Abb.	Thamnolic acid, usnic acid, decarboxythamnolic acid (tr)
Bario 2	*Crocynia* sp.	No lichen substances
Bario 9	*Dictyonema sericeum* (Sw) Berk.	No lichen substances
Bario 89	*Heterodermia leucomclos* ssp. *Boryi* (fee) Swinc. & Kro	Atranorin, zeorin, unknown triterpene
Bario 15 Bario 45	*Heterodennia leucomelos* (L.) Poelt ss . *leucomelos*	Atranorin, zeorin, norstictic acid, salazinic acid, purple (±), unknown triterpene (±)
Bario 16	*Lobaria crassior* Vain.	Gyrophoric acid, 4-O-methylgyrophoric acid
Bario 4 Bario 29	*Lobaria discolor* (Bory in Del.) Hue	Gyrophoric acid
Bario 7 Bario 25 Bario 50	*Lobaria isidiophora* Yoshim.	Stictic acid, constictic acid, gyrophoric acid, norstictic acid (tr)
Bario 31	*Lobaria pseudopulmonaria* Gyeln.	Thelephoric acid, norstictic acid, stictic acid, constictic acid, cryptostictic acid, salazinic acid, mene azziaic acid, unknown triter encs
Bario 36	*Parmeliella brisbanensis* (Knight) PM.Jor . & D. Gall.	No lichen substances

Bario 18 Bario 33	*Parmotrema acrotrychum* (Kurok.) Streim.	Atranorin, fumarprotocetrarbc acid, succinpro tocetraric acid, chloroatranorin, protocetraric acid (tr), protolichesterinic acid, lichesterinic acid
Bario 24	*Parmotrenta* cf. *cristiferum* (Taylor) Hale	Atranorin, chloroatranorin, salazinic acid, consalazinic acid, unknown
Bario 6	*Pannotrema subantoldii* (des Ab-bayes) Hale	Atranorin, chloroatranorin, protocetraric acid, rotolichesterinic acid, lichesterinic acid
Bario 17	*Parrnotrema subcorallintim* (Hale) Hale	Atranorin, chloroatranorin, protocetraric acid, rotolichesterinic acid, lichesterinic acid
Bario 10	*Parmotrema sulphuratum* (Nees & Flot.) Hale	Vulpinic acid, unknown fatty acid
Barb 47	*Physcidia cylindrophora* (Taylor) Hue	Atranorin, homosekikaic acid (major), Hyper-sekikaic acid (minor)
Bario 40 Bario 42	*Pseudocyphellaria crocata* (L.) Vain.	Calycin, pulvic dilactone, tenuiorin, methyl gyrophorate, stictic acid, constictic acid, cryptostictic acid, hopane-6cx, 711, 22-triol
Bario 26	*Relicina ahstrusa* (Vainio) Hale	Usnic acid, norstictic acid, connorstictic acid
Barb 30A	*Relicina* luteoviridis (Kurok.) Hale	Usnic acid, gyrophoric acid
Bario 30B	*Relicina malesiana* (Hale) Hale	Usnic acid, fumarprotocetraric acid (major), Protocetratic acid
Barb 49	Relicina sublanea (Kurok.) Hale	Usnic acid, protocetraric acid
Bario 5 Bario 8	*Relicinopsis intertexta* (Mont. & v.d. Bosch) Elix & Verdon	Usnic acid, protocetraric acid
Barb 20	*Rimelia reticulata* (Taylor) Hale & Fletcher	Atranorin, chloroatranorin, consalazinic

Bario 35	*Usnea baileyi* (Stirt.) Zahlbr.	Usnic acid, salazinic acid, norstictic acid, protocetraric acid (tr), eumetrins A, A_2, B

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