

Notes on the chemical variation of the lichenized Ascomycota *Cladia aggregata* (Cladoniaceae) in the states of Paraná and Santa Catarina, Brazil

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ABSTRACT

The chemical compounds of *Cladia aggregata* from the states of Paraná and Santa Catarina were analyzed, resulting in five chemotypes. The chemotypes are as follows: barbatic and 4-O-demethylbarbatic acid; barbatic, 4-O-demethylbarbatic, and homosekikaic acid; barbatic, 4-O-demethylbarbatic and diffractaic, or barbatic and diffractaic acid; barbatic, 4-O-demethylbarbatic, and fumarprotocetraric acid; and barbatic, 4-O-demethylbarbatic, and stictic acid.

Key words: barbatic acid, diffractaic acid, fumarprotocetraric acid, homosekikaic acid, stictic acid

Cladia aggregata (Sw.) Nyl. is a highly variable species, and, according to Ahti (2000), its total chemical variation is more extensive than is that of other Cladoniaceae. In a revision of the genus *Cladia*, Filson (1981) treated this species in a broad sense and reported 21 compounds. Kantvilas & Elix (1999) revised the *C. aggregata* complex in Tasmania and identified six chemotypes in *C. aggregata sensu stricto*. Information on the chemical composition of Brazilian specimens of *C. aggregata* can be found in Filson (1981), Ahti *et al.* (1993), Fleig *et al.* (1995), Ahti (2000), and Cruz *et al.* (2009).

The study is based on 41 specimens from the Herbarium of the Federal University of Paraná and the Curitiba Municipal Botanical Museum (codes, UPCB and MBM, respectively). The chemical constituents were identified using standardized methods for thin layer chromatography (Culberson & Ammann 1979). The presence of diffractaic acid was confirmed by thin layer chromatography and nuclear magnetic resonance at the Federal University Mato Grosso do Sul, located in the state of Mato Grosso do Sul, Brazil.

All of the specimens contained barbatic acid, as a constant chemical constituent, and at least one other substance. We identified five chemotypes:

1. barbatic and 4-O-demethylbarbatic acid
2. barbatic, 4-O-demethylbarbatic, and homosekikaic acid

3. barbatic, 4-O-demethylbarbatic and diffractaic, or barbatic and diffractaic acid
4. barbatic, 4-O-demethylbarbatic, and fumarprotocetraric acid
5. barbatic, 4-O-demethylbarbatic, and stictic acid

Most of the analyzed specimens (68.3%) were chemotype 1. This result agrees with those reported by Kantvilas & Elix (1999) and Ahti (2000).

Chemotype 2 accounted for 22% of the specimens. This was an unexpected result, because homosekikaic acid is a rare compound in *Cladia aggregata* and was not found in specimens from Chile (Ahti & Kashiwadani 1984), New Zealand (Galloway 1985), Melanesia (Stenroos 1988), Tasmania (Kantvilas & Elix 1999), Australia (Filson 1992), and Malaysia (Zakaria *et al.* 2000). Although chemotype 2 was detected in specimens from Brazil (Filson 1981), it was not found in a study of various neotropical samples (Ahti 2000).

Chemotype 3 occurred in 4.9% of the samples. Ahti (2000) identified diffractaic acid only in specimens from Uruguay and Venezuela. The depside barbatic acid, the major compound in the other four chemotypes, was found in small quantities in chemotype 3, and there was one specimen in which 4-O-demethylbarbatic acid was not detected.

Only 2.4% of the studied specimens belonged to chemotype 4. The production of fumarprotocetraric acid was

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reported by Fleig *et al.* (1995) in specimens from the Brazilian state of Rio Grande do Sul but was regarded as very rare. Ahti (2000) detected this compound in specimens from Mexico to Uruguay but noted it was produced in greater concentrations only in specimens from Ecuador and Chile.

Like chemotype 4, chemotype 5 was found in only 2.4% of the specimens. According to Ahti (2000), such specimens are common to the Andean region of Colombia and Venezuela, as well to the Brazilian states of Bahia and Minas Gerais.

No correlation was observed between the morphology of the specimens and the chemotypes 1, 2, 3 or 5. The specimens were morphologically homogeneous, with sterile pseudopodetia of up to 9 cm in height and 0.3-1.5 mm in thickness. However, the chemotype 4 specimen had more robust sterile pseudopodetia (up to 11 cm in height and 3.0 mm in thickness), as was also reported by Ahti (2000) for Ecuadorian specimens. It is possible that the specimens belonging to chemotype 4 represent a different species within the *Cladia aggregata* complex in the neotropics, but more advanced studies are needed, including ecological and molecular analyzes.

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