The Biflavonoid Pattern of the Moss *Bartramia ithyphylla* (Bartramiaceae, Musci)

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From *Bartramia ithyphylla* the following five biflavonoids were isolated: philonotisflavone, 2,3-dihydrophilonotisflavone, dieranolomin, 5',3''-dihydroxyamentoflavone and 5'-hydroxyamentoflavone.

*Bartramia* Hedw. is a large moss genus of about 100 species and three sections (Corley et al., 1981). During a study of the flavonoid patterns of the Bartramiaceae by TLC and HPLC (López-Sáez, 1994), we found that our standard chromatograms of *Bartramia ithyphylla* contain a new biflavonoid unknon in the family. This compound was identified by its FD-MS spectra and NMR spectra, as well as by cochromatography with authentic samples of 5'-OH-amentoflavone, and has been reported from Mniaceae (Geiger et al., 1988; Anhut et al., 1989) and Hylcomiaceae (Seeger et al., 1990). This result confirm the existence of three sections in the genus *Bartramia*: sec. *Bartramia*, with macrocyclic biflavonoids and triflavonoids (Seeger et al., 1991, 1992; Salm et al., 1993); sec. *Strictidium* with triflavonoids one of them cyclic (López-Sáez, 1994; Geiger et al., 1994) and finally, sec. *Ithyphyllea* with *Bartramia ithyphylla* is included, without cyclic flavonoids but with biflavonoids containing an apigenin moiety.

**Experimental**

**Plant Material**

Gametophytic material of *Bartramia ithyphylla* Brid. was collected from National Park of Aigües Tortes, Lérida (Spain), 2.11.1991, leg. et det. J.A. López-Sáez and Puerto de Canencia, Madrid (Spain), 10.12.1988, leg. et det. M.E. Ron. Voucher specimens are deposited in the Herbarium of the Department of Plant Biology, Faculty of Biology, Complutense University of Madrid ("MACB").

**Extraction and isolation**

120 g air-dried plant material (freed from foreign matter) was extracted three times with MeOH:H2O (8:2) 5 l each and twice with 4 l Me2CO:H2O (8:2). To eliminate chlorophylls the combined extracts were evaporated and the residue subjected to a four step Craig distribution between the upper and lower phases of DMF/H2O/ET2O (4:1:8). The combined lower phases were reduced in vacuo to a thin syrup (about 100 ml). After addition of 60 ml dry polyamide-6 powder it was diluted with 1 l water. The resulting suspension was cautiously poured on top of a 3-l polyamide-6-column (wet packed). The column was eluted with 2 l each of Me2CO:H2O (1:9; 2:8; 3:7; 4:6; 5:5; 6:4; 7:3) and 4 l (8:2).

The compounds were eluted as follows: 1, 2, 2 + 3, 3, 4, 4 + 5, 5.

Further separation and purification was done by CC on Sephadex LH 20 with Me2CO:H2O:MeOH (2:1:1). Yields: 200 mg of 2,3-dihydrophilonotisflavone (1); 80 mg of philonotisflavone (2); 65 mg of dieranolomin (3); 120 mg of 5'-hydroxyamentoflavone (4); and 25 mg of 5',3''-dihydroxyamentoflavone (5).

1H NMR spectroscopy: Bruker AM 400, 400 MHz, DMSO-d6, ambient temperature (Table I).

13C NMR spectroscopy: Bruker AM 400, 100 MHz, DMSO-d6, ambient temperature.

Mass spectra were recorded by FAB-technique (negative mode) on Hewlett Packard 5970 (70 eV).

**Acknowledgements**

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Table I. PMR-spectra of 1–5. (DMSO-d6, ambient temperature, 400 MHz). In parentheses the coupling constants in [Hz].

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<tr>
<td>H-3</td>
<td>3.27 dd (17; 14)</td>
<td>6.04 s</td>
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* Main component.


