

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

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Z. Naturforsch. **50c**, 311–312 (1995);
received October 31, 1994/January 23, 1995

Bartramiaceae, *Bartramia ithyphylla* Brid., Biflavonoids

From *Bartramia ithyphylla* the following five biflavonoids were isolated: philonotisflavone, 2,3-dihydrophilonotisflavone, dicranolomin, 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* contains a new biflavonoid unknown in the family. This compound was identified by its FD-MS spectra and NMR spectra, as well as by cochromatography with authentic samples as 5'-OH-amentoflavone, and has been reported from Mniaceae (Geiger *et al.*, 1988; Anhut *et al.*, 1989) and Hylocomiaceae (Seeger *et al.*, 1990). This result confirms 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. *Ithyphyllae* with *Bartramia ithyphylla* is included, without cyclic flavonoids but with biflavonoids that 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 dicranolomin (**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

The authors are pleased to acknowledge the Community of Madrid for financial support of this work.

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

	1 *	2	3	4	5
H-2	5.01 dd (12; 2) [H-3a]	—	—	—	—
H-3	3.27 dd (17; 14) [H-3a] 2.59 dd (18; —) [H-3b]	6.04 s	6.04 s	6.78 s	6.64 s
H-6	5.78 d (2)	5.73 d (2)	5.96 d (2)	6.26 d (2)	6.18 d (2)
H-8	5.43 d (2)	6.07 d (2)	6.08 d (2)	6.47 d (2)	6.42 d (2)
H-2'	—	—	—	7.56 d (2)	7.48 d (2)
H-5'	6.91–7.10 m	7.02 m	6.94 d (8)	—	—
H-6'	6.91–7.10 m	7.24 d (8)	7.18 d (8)	7.60 d (2)	7.49 d (2)
H-3''	6.62 s	6.60 s	6.68 s	6.85 s	6.68 s
H-6''	6.35 s	6.26 s	—	6.43 s	6.37 s
H-8''	—	—	6.54 s	—	—
H-2'''	6.91–7.10 m	7.02 m	7.42 d (2)	7.66 d (9)	7.06 d (2)
H-3'''	—	—	—	6.77 d (9)	—
H-5'''	6.75 d (8)	6.74 d (8)	6.89 d (8)	6.76 d (9)	6.67 d (8)
H-6'''	6.91–7.10 m	7.02 m	7.43 dd (9; 2)	7.65 d (9)	7.04 dd (2; 8)
OH-5	12.05 s	12.72 s	12.78 s	13.08 s	13.00 s
OH-5''	—	13.01 s	13.13 s	12.97 s	13.13 s

* Main component.

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