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

José Antonio López-Sáez,
María José Pérez-Alonso and
Arturo Velasco-Negueruela

Departamento de Biología Vegetal I, Facultad de Biología, Universidad Complutense, 28040 Madrid, Spain

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 unknon 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 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. *Ithyphyllae* wich *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").

Reprint requests to Dr. J. A. López-Sáez.

Extraction and isolation

120 g air-dried plant material (freed from foreign matter) was extracted three times with MeOH:H_2O (8:2) 5 l each and twice with 4 l Me_2CO:H_2O (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/H_2O/Et_2O (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 Me_2CO:H_2O (1:9; 2:8; 3:7; 4:6; 5:5; 6;4; 7:3) and 4 l (8:2).

The compouds 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 Me_2CO:H_2O: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-d_6, ambient temperature (Table I).

^{13}C NMR spectroscopy: Bruker AM 400, 100 MHz, DMSO-d_6, 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.

0939–5075/95/0300–0311 $ 06.00

Table I. PMR-spectra of **1–5.** (DMSO-d_6, 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.

Anhut S., Seeger T., Biehl J., Zinsmeister H. D. and Geiger H. (1989), Phytochemical studies of the moss species *Plagiomnium elatum* and *Plagiomnium cuspidatum*. Journ. Hattori Bot. Lab. **67**, 377–382.

Corley M. F. V., Crundwell A. C., Dull R., Hill M. O. and Smith A. J. E. (1981), Mosses of Europe and the Azores; an annotated list of species, with synonyms from the recent literature. J. Bryol. **11**, 609–689.

Geiger H., Anhut S. and Zinsmeister H. D. (1988), Biflavones from some mosses. Z. Naturforsch. **43c**, 1–4.

Geiger H., Voigt A., Seeger T., Zinsmeister H. D., López-Sáez J.A., Pérez-Alonso M. J. and Velasco-Negueruela A. (1994), Cyclobartramiatriluteolin, a unique new Triflavonoid from *Bartramia stricta*. Phytochemistry (in preparation).

López-Sáez J. A. (1994), Flavonoides en Bartramiaceae Schwaegr. (Musci, Bryophyta): Aspectos Quimiosistemáticos y Actividad Biológica. Tesis Doctoral. Universidad Complutense. Madrid.

Salm R., Seeger T. and Zinsmeister H. D. (1993), Die Biflavonoidmuster des Laubmooses *Bartramia halleriana*. Z. Naturforsch. **48c**, 531–532.

Seeger T., Geiger H. and Zinsmeister H. D. (1991), Bartramiaflavone, a macrocyclic biflavonoid from the moss *Bartramia pomiformis*. Phytochemistry **5**, 1653–1656.

Seeger T., Geiger H. and Zinsmeister H. D. (1992), Isolierung und Strukturaufklärung von Bartramia-Triluteolin, Bartramiasäure und einigen Biflavonoiden aus dem Laubmoos *Bartramia pomiformis*. Z. Naturforsch. **47c**, 527–530.

Seeger T., Zinsmeister H. D. and Geiger H. (1990), The biflavonoid pattern of *Rhytydiadelphus squarrosus* (Hedw.) Warnst. Z. Naturforsch. **45c**, 583–586.