The Biflavonoid Pattern of the Moss *Bartramia mossmanniana* (*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. **50 c,** 895–897 (1995); received June 28/September 19, 1995

Bartramiaceae, *Bartramia mossmanniana* C. Müll., Biflavonoids

From *Bartramia mossmanniana* the following five biflavonoids were isolated: bartramiaflavone, anhydrobartramiaflavone, philonotisflavone, 2,3-dihydrophilonotisflavone and 5′,3‴-dihydroxyamentoflavone.

Among the 49 species of Bartramiaceae family that are known from Peru (Hegewald and Hegewald, 1975, 1977, 1985; Griffin, 1984a, 1984b; Griffin and Hegewald, 1986), *Bartramia mosmanniana* is one of the more interesting species from a chemotaxonomic point of view. *Bartramia mosmanniana* is a typical moss from the Austral-Antartic flora (Herzog, 1926), whose sporophyte is similar to *Bartramia halleriana* with a setae 3–5 mm long (Engler, 1924).

During a study of the biflavonoid patterns of the *Bartramia* genus section Bartramia, by TLC and HPLC (López-Sáez, 1994), we found that our standard chromatograms of *Bartramia mosmanniana* containing the same biflavonoid composition known in the section. These results confirm that the synthesis of macrocyclic biflavonoids (Figs. 1–2) only occurs in the *Bartramia* section of the genus *Bartramia* (Seeger *et al.*, 1991; Seeger *et al.*, 1992; Salm *et al.*, 1993).

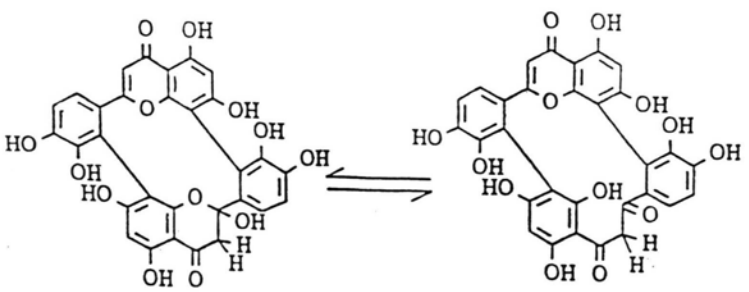

Fig. 1. Bartramiaflavone (**1**).

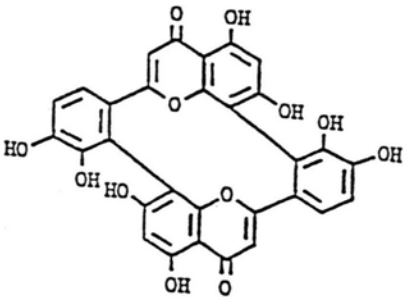

Fig. 2. Anhydrobartramiaflavone (**4**).

Experimental

Plant material

Gametophytic material of *Bartramia mossmanniana* C. Müll. was collected from Apurimac, Pass Socchacasa, 3000 m (Peru), 5.10.1989, leg. et det. E. Hegewald. Voucher specimens are deposited in the Herbarium of the Department of Plant Biology, Faculty of Biology, Complutense University of Madrid ("MACB").

Extraction and isolation

80 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) (ambient temperature). 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 com-

0939–5075/95/1100–0895 $ 06.00 D

Table I. PMR-spectra of **1–5** ($DMSOd_6$, ambient temperature, 400 MHz). In parenthese the coupling constants in [Hz].

H*	1*	1**	2***	3	4	5
2	–	–	5.02 dd (12; 2)	–	–	–
3a	2.34 d (17)	3.40 d (15)	3.29 dd (17; 14)	6.06 s	6.27 s	6.64 s
3b	2.93 d (17)	5.38 d (15)	2.61 dd (18; –)	–	–	–
6	5.81 s	5.90 s	5.78 d (2)	5.74 d (2)	5.75 s	6.16 d (2)
8	–	–	5.44 d (2)	6.08 d (2)	–	6.41 d (2)
2′	–	–	–	–	–	7.48 d (2)
5′	6.77 d (8)	6.84 d (8)	6.92–7.11 m	7.05 m	6.74 d (8)	–
6′	7.13 d (8)	7.38 d (8)	6.92–7.11 m	7.25 d (8)	6.82 d (8)	7.47 d (2)
3″	6.25 s	6.31 s	6.62 s	6.63 s	6.26 s	6.68 s
6″	5.76 s	5.76 s	6.37 s	6.27 s	5.74 s	6.36 s
8″	–	–	–	–	–	–
2‴	–	–	6.92–7.11 m	7.05 m	–	7.03 d (2)
5‴	6.74 d (8)	6.66 d (8)	6.75 d (8)	6.75 d (8)	6.74 d (8)	6.66 d (8)
6‴	6.80 d (8)	6.81 d (8)	6.92–7.11 m	7.05 m	6.81 d (8)	7.04 dd (2; 8)
OH-2	7.36 s	–	–	–	–	–
OH-5	12.06 s	12.84 s	12.06 s	12.76 s	12.66 s	12.99 s
OH-5″	12.78 s	12.96 s	–	13.04 s	12.66 s	13.12 s

* Ciclo tautomer; ** Oxo tautomer; *** Main component.

bined 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, 5**.

Further separation and purification was done by CC on Sephadex LH 20 with Me_2CO:H_2O:-MeOH (2:1:1).

Yields: 325 mg of bartramiaflavone (**1**); 175 mg of 2,3-dihydrophilonotisflavone (**2**); 85 mg of philonotisflavone (**3**); 10 mg of anhydrobartramiaflavone (**4**) and 18 mg of 5′,3‴-dihydroxiamentoflavone (**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 "Ministerio de Educación y Ciencia" for financial support of this work.

Engler A. (1924), Die Natürlichen Pflanzenfamilien, Duncker & Humblot, Berlin.

Griffin D. III. (1984a), A comparison of *Breutelia subarcuata* (C. Muell.) Schimp. in Besch. and *B. chrysea* (C. Muell.) Jaeg. in Latin America. The Bryologist **87,** 233–237.

Griffin D. III. (1984b), Studies on Colombian cryptogams XXII: The *Breutelia subarcuata* complex in Colombia and neighboring areas. Acta Bot. Neerl. **33,** 275–282.

Griffin D. III. and Hegewald E. (1986), A collection of *Bartramiaceae* from Peru. Journ. Hattori Bot. Lab. **60,** 159–165.

Hegewald E. and Hegewald P. (1977), Eine Moossammlung aus Peru. I. Nova Hedwigia **28,** 731–758.

Hegewald E. and Hegewald P. (1985), Eine Moossammlung aus Peru. II. Nova Hedwigia **41,** 555–563.

Hegewald P. and Hegewald E. (1975), Verzeichnis der Laubmoose von Peru nach Literaturangaben. J. Hattori Bot. Lab. **39,** 39–66.

Herzog, Th. (1926). Geographie der Moose, Gustav Fischer-Verlag, Jena.

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.