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CYCLOBARTRAMIATRILUTEOLIN, A UNIQUE TRIFLAVONOID FROM *BARTRAMIA STRICTA**

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Key Word Index—*Bartramia stricta*; Bartramiaceae; musci; cyclobartramiatriluteolin; bartramiatriluteolin; philonotisflavone; dicranolomin; 5′3‴-dihydroxyamentoflavone; 5′3‴-dihydroxyrobustaflavone.

Abstract—Cyclobartramiatriluteolin, a new triflavone in which three head-to-tail linked luteolin moieties form an 18-membered macrocycle, has been isolated from *Bartramia stricta*. Its structure was elucidated spectroscopically. In addition, five known bi- and triflavonoids have been isolated and identified.

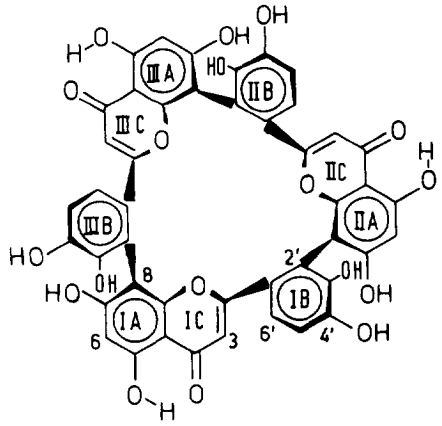
INTRODUCTION

During a chemosystematic survey of the moss family Bartramiaceae [1] it was realized, that *Bartramia stricta* contains some hitherto unknown flavonoids. This prompted us to study this species in detail. Separation of an aqueous acetone extract from *B. stricta* as described in the Experimental yielded the new cyclobartramiatriluteolin (**1**), and a mixture of at least three other new triflavonoids, that is still under investigation. Furthermore, the known flavonoids bartramiatriluteolin (**2**), philonotisflavone (**3**), dicranolomin (**4**), 5′,3‴-dihydroxyamentoflavone (**5**) and 5′,3‴-dihydroxyrobustaflavone (**6**) were isolated and identified by their NMR spectra [2, 3] and co-chromatography with authentic material from *B. pomiformis* [2] and *Hylocomium splendens* [4].

RESULTS

The main subject of the present communication is the elucidation of the structure of **1**. The ^{13}C NMR spectrum exhibited only 15 signals, the chemical shifts of which are very close to those observed in the spectrum of anhydrobartramiaflavone (**7**) (Table 1, [5]). Compound **7** is a cyclobiluteolin, that has a two-fold axis of symmetry and shows, therefore, only 15 instead of 30 ^{13}C resonances. The M_r of **1** and **7** were, however, different: M_r of **7**, 568 (= 2 × 284) and M_r of **1**, 852 (= 3 × 284). Thus, **1** must be a cyclo-triluteolin having a three-fold axis of symmetry.

The location of the interflavonyl linkages of **1** follows, as with **7**, from a comparison of its NMR spectra with those of its monomer, luteolin (**8**) (see Table 1): an uncoupled proton signal at δ6.32 correlated with the C-6 signal at δ98.0 and a downfield shift of the C-8 resonance by 9 ppm relative to **8** define C-8 as one bridgehead. The other bridgehead was shown to be C-2′ by the *ortho* coupled H-5′ and H-6′ signals and a downfield shift of the C-2′ resonance relative to **8**. The only way in which the three luteolin units can be united via their C-8 and C-2′ to a symmetrical molecule is by a 8 → 2′ linkage; all other combinations do not lead to a molecule with a three-fold axis of symmetry. Formula 1 shows this rather unusual molecule in top view. In side view its overall shape is reminiscent of an hour glass: at the top the B-rings are



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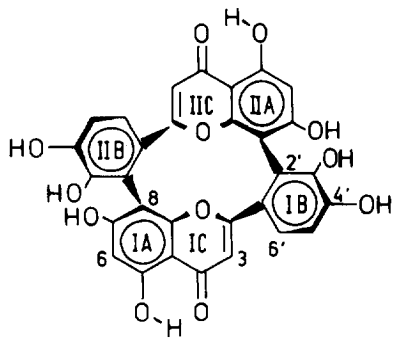

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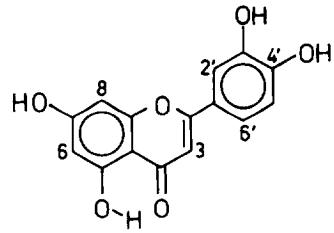

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Table 1. ^{13}C and ^{1}H NMR spectral data of compound **1** and two related compounds in DMSO-d_6 at ambient temp. with 100 and 400 MHz, respectively, because of symmetry assignments for **1** and **7** are given only for one of the moieties

	1*		7* [3, 5]		8 [5]	
Position	C	H	C	H	C	H
2	164.8	—	167.1	—	164.5	—
3	106.7	5.93 *s*	108.9	5.74 s	103.3	6.69 *s*
4	181.1	—	181.6	—	182.2	—
5	160.4	—	160.4	—	162.1	—
6	98.0	6.32 *s*	98.6	6.26 *s*	99.2	6.22 d^m
7	162.4	—	163.4	—	164.7	—
8	103.3	—	103.1	—	94.2	6.47 d^m
9	154.6	—	154.6	—	157.9	—
10	102.8	—	102.7	—	104.2	—
1′	124.9	—	125.5	—	122.1	—
2′	118.6	—	119.1	—	113.8	7.43 d^m
3′	144.2	—	144.4	—	146.2	—
4′	147.6	—	147.0	—	150.1	—
5′	114.6	6.69 d^o	113.9	6.80 d^o	116.4	6.92 d^o
6′	118.9	6.34 d^o	118.7	6.73 d^o	119.3	7.44 dd^{om}

*^{13}C and ^{1}H signals correlated by the 'inverse' technique.

slanting somewhat outward and at the base the A- and C-rings do the same.

In accordance with this structure also are the chemical shifts of the H-3,5′ and 6′ signals of **1**. These signals are observed at much higher field than the corresponding signals of luteolin (**8**) because these protons are situated within the shielding zones of the neighbouring luteolin moieties. Similar effects are also observed with anhydrobartramiaflavone (**7**) [3].

EXPERIMENTAL

Bartramia stricta Brid., gametophytes containing a few sporophytes, was collected and identified by J.A.L.-S. at Villa del prado near Madrid. A voucher is deposited at MACB (J.A. Lopez-Saez, 22 December 1992).

Extraction and CC on polyamide 6 with a H_2O–Me_2CO gradient were performed as described earlier [6]. The sequence of elution from the polyamide column was **3**, **1**, **4**, **2**, a mixture of further triluteolins, **5**, and **6**. Since there was considerable overlapping, mixed fractions were further separated by CC on Sephadex LH20 with the eluents Me_2CO–MeOH–H_2O (2:1:1) and MeOH–H_2O (4:1). With these systems the order of elution was **1** + **2** + other triluteolins, **3**, **4**, **5**, **6** and **2**, **3**, **4**, **1**, respectively. From 200 g air-dried *B. stricta* were isolated by a combination of these methods 70 mg **1**, 20 mg **2**, 21 mg **3**, 9 mg **4**, 26 mg **5**, 5 mg **6**, and about 100 mg of a mixture of several triluteolins, that is still under investigation. The M_r of **1** was determined by laser induced microprobe mass analysis (LAMMA) using nicotinic acid amide as matrix.

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