Flavone-C-Glycosides from the Mosses *Plagiomnium elatum* and *Plagiomnium cuspidatum**

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In *Plagiomnium elatum* the new di-C-glycosides 6-C-β-D-glucopyranosyl-8-C-α-L-rhamnopyranosyl-luteolin (Elatin) and 6-C-hexosyl-8-C-rhamnosyl-chrysoeriol were detected. Furthermore four known flavone-C-glycosides were identified. The main glycosides of *Plagiomnium cuspidatum* are 6-C-glucosyl-7-O-glucosides of apigenin, luteolin and chrysoeriol respectively.

Introduction

Since the first phytochemical studies on *Mnium* species, when Kozlowski [1] detected saponarin in *Mnium cuspidatum* by a chemical reaction with iodine potassium iodide solution, several reports on the occurrence of flavone-C-glycosides in this species and in *Mnium affine* [2–4] were mainly based on the results of paper chromatographic screenings.

According to Koponen's "Generic revision of Mniaceae" most of the screened species are allocated in the genus *Plagiomnium* – [5]. Although he compared flavonoid patterns (TLC) of *Plagiomnium* and *Rhizomnium* species to support his thesis on species pairs in these genera [6], until now only for two *Plagiomnium* species and for two *Rhizomnium* species the structure elucidation of flavonoid glycosides has been reported.

In *Plagiomnium undulatum* mainly 6,8-di-C-glycosides of apigenin were found and additionally saponarin and one not fully identified chrysoeriol-6,8-di-C-glycoside [7, 8].

Plagiomnium affine mainly contains C/O-glycosides of the luteolin type [9].

In contrast for *R. magnifolium* and *R. pseudopunctatum* only glucuronides of different flavone aglycones are known [10].

In *Plagiomnium elatum* and *P. cuspidatum* some new biflavonoids were found [11, 12].

Here the structure elucidation of the main glycosides from these species is reported.

Results

As confirmed by two-dimensional TLC screening of many samples the gametophytes of each species seem to produce characteristic and constant flavonoid patterns [13].

The structures of the identified *C-glycosides* of *Plagiomnium elatum* (**Pe 1**–**Pe 6**) are listed in Fig. 1. Their chromatographic and UV spectroscopic data are given in Tables I and II. The NMR and mass spectroscopical data are presented in Tables III–V.

Except for **Pe 4** all *Plagiomnium elatum* C-glycosides show the characteristic fluorescence and UV spectra of luteolin as common aglycone unit.

Upon acid treatment of the glycosides neither luteolin nor any sugar could be detected. Since in all cases additional spots appeared on TLC plates after 2-dimensional development Wessely-Moser rearrangements [14] had occurred.

Chromatographic and UV spectroscopic properties of the isomer of **Pe 1** originating from acid treatment were identical with **Pe 2** and *vice versa*. The FD/MS, PMR and ^{13}C NMR data confirm the structure of orientin for **Pe 1** and isoorientin for **Pe 2** respectively.

Whereas isoorientin is already known from *Plagiomnium affine* [9], orientin has not been identified before in any bryophyte [15].

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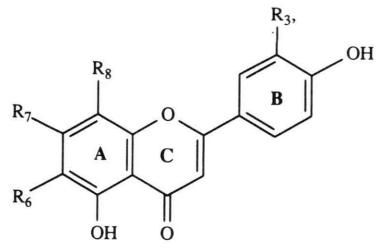
Table I. Thin layer chromatographic data of the flavone-C-glycosides from *Plagiomnium elatum* (**Pe 1–Pe 6**) and *Plagiomnium cuspidatum* (**Pc 1–Pc 3**).

Compound	**Pe 1**	**Pe 2**	**Pe 3**	**Pe 4**	**Pe 5**	**Pe 6**	**Pc 1**	**Pc 2**	**Pc 3**
Colour reactions									
$UV_{366/254nm}$	v	v	v	v	v	v	v	v	v
UV + NH_3	ye-gr	ye-gr	gr	gr-ol	ye-gr	ye-gr	ye-gr	ye-gr	ye-gr
UV + NA	ye	ye	ye-or	gr	ye	ye	ye	d-oliv	oliv-gr
UV + BR	dark	dark	dark	gr	dark	dark	dark	ye-gr	ye-gr
Sorbent/solvent system	TLC hR_f values								
Cellulose									
HOAc–H_2O 15:85	6	23	40	45	25	26	40	48	56
HOAc–H_2O 40:60	26	54	75	77	53	53	70	77	79
TBA = BuOH(3)–HOAc–H_2O 3:1:1	18	36	23	25	6	6	14	20	33
BAW = BuOH(1)–HOAc–H_2O 4:1:5 (upper layer)	28	40	36	38	18	20	37	39	42
BEW = BuOH(2)–HOAc–H_2O 14:1:5	33	63	–	–	12	13	32	32	38
AEW = *n*-pentanol–HOAc–H_2O 2:1:1	28	45	–	–	20	19	34	40	48
Polyamide P_6									
AEW = *n*-pentanol–HOAc–H_2O 2:1:1	38	53	–	–	49	49	–	–	–
WEMA = H_2O–MeCOEt–MeOH–2,4-pentadione 13:3:3:1	22	18	60	65	56	45	64	72	69
EtOAc–MeCOEt–HCOOH–H_2O 5:3:1:1	26	46	20	23	4	4	12	24	24
Silica (KG 60 F_{254})									
EtOAc–MeCOEt–HCOOH–H_2O 5:3:1:1	54	–	–	–	12	12	15	17	19
EtOAc–HOAc–H_2O 67:19:20	50	46	23	28	16	17	13	19	19
EtOAc–HCOOH–H_2O–MeCOEt 3:6:1:2	57	63	54	57	49	50	–	–	–

Na = Naturstoffreagenz A.
BR = Benedict's Reagenz.

Compounds **Pe 3** and **Pe 4** could be finally separated on a Sephadex LH 20 column with MeOH. Because of their high mobility in polar solvent systems and the Wessely-Moser rearrangement for both compounds an asymmetric 6,8-di-C-glycosylation was expected. The observed signal m/e = 576 in the FD mass spectrum of **Pe 3** therefore would correspond to the molecular ion of a di-C-glycosyl-luteolin after loss of H_2O [$M^+ - 18$].

In the PMR spectrum the observed ABX system of the B-ring protons at C-2′, 5′ and 6′ is comparable to those of **Pe 1** and **Pe 2.** Whereas the singulett for H-3 at 6.69 ppm is almost identical with values of **Pe 1** and **Pe 2,** there were no signals for protons at C-6 or C-8 observed, but two anomeric protons. The doublett at 4.60 ppm with the coupling constant (J = 10 Hz) is significant for β-configurated and C-linked glucopyranose, while the broad singulett at 5.23 ppm represents the anomeric proton of a rhamnose unit which is characterized additionally by the doublett (1.28 ppm; J = 6 Hz) of its methyl group (Table V).



	$R_{3'}$	R_7	R_8	R_6
Pe 1	OH	OH	β-D-glucopyranosyl	–
Pe 2	OH	OH	–	β-D-glucopyranosyl
Pe 3	OH	OH	α-L-rhamnopyranosyl	β-D-glucopyranosyl
Pe 4	OCH_3	OH	rhamnopyranosyl	hexopyranosyl
Pe 5	OH	OH	β-D-glucopyranosyl	β-D-glucopyranosyl
Pe 6	OH	OH	hexopyranosyl	xylopyranosyl
Pc 1	OH	O-β-D-glucopyranose	–	β-D-glucopyranosyl
Pc 2	OCH_3	O-β-D-glucopyranose	–	β-D-glucopyranosyl
Pc 3	H	O-β-D-glucopyranose	–	β-D-glucopyranosyl

Fig. 1. Substitution patterns of the identified C-glycosides from *Plagiomnium elatum* (**Pe**) and *Plagiomnium cuspidatum* (**Pc**).

Table II. UV spectroscopic data (nm) of the flavone-C-glycosides **Pe 1–Pe 6** from *Plagiomnium elatum* and **Pc 1–Pc 3** from *Plagiomnium cuspidatum*.

	Pe 1	**Pe 2**	**Pe 3**	**Pe 4**	**Pe 5**	**Pe 6**
MeOH	255–268– 290 sh–349	243 sh–256 270–294 sh 349	259–271 292 sh–350	244 sh–273 346	256 sh–270 287 sh–349	257 sh–270 290 sh–348
MeOH + NaOMe	234 sh–267 277 sh–334 sh 405	237 sh–267 276 sh–331 sh 408	239 sh–269 278 sh–331 sh 410	264 sh–280 333 sh–411	239 sh–268 280 sh–336 sh 410	267–280 sh 334 sh–409
MeOH + $AlCl_3$	273–302– 326 sh–365 sh 423	234 sh–275 302 sh–331 427	275–304 sh 330–429	236 sh–262 sh 276–304– 365–396 sh	240 sh–278 305 sh–329 426	278–303 sh 336 sh–427
MeOH + $AlCl_3$ HCl	231–260– 274 sh–297 357–383 sh	232 sh–263 sh 277–297 sh 359–383 sh	262–280 sh 299 sh–357 393 sh	236 sh–258 286–300 sh 356–390 sh	234 sh–259 sh 277–299 sh 357–389 sh	261 sh–278 297 sh–356 384 sh
MeOH + NaOAc	269–318 sh 383	272–324– 389	243 sh–271 326 sh–365 407	280–320 378	241 sh–269 sh 281–323–385	278–327 sh 372
MeOH + NaOAc H_3BO_3	262–372	262–375	263–375	273–281 sh 351	264–376	264–374
	Pc 1	**Pc 1,** Hyd	**Pc 2**	**Pc 2,** Hyd	**Pc 3**	**Pc 3,** Hyd
MeOH	259–270– 351	256–269– 350	254–272 345	253 sh–271 345	272–332	271–335
MeOH + NaOMe	271–277 sh 299 sh–400	267–272 sh 338 sh–407	278–298 sh 306 sh–400	261 sh–280 275 sh–336 409	273–278 sh 310–357 sh 387	280–330 398
MeOH + $AlCl_3$	276–297 sh 325–360 sh 428	275–299 sh 329–425	278–298 sh 368–384 sh	265 sh–278 298 sh–364 390 sh	278–302 355–371 sh	278–302 355–375 sh
MeOH + $AlCl_3$ HCl	263 sh–276 296 sh–361 386 sh	264 sh–279 295 sh–359 379 sh	261 sh–279 296 sh–359 376 sh	261 sh–280 295 sh–356 382 sh	279–301 346–372 sh	277–301 346–375 sh
MeOH + NaOAc	265–388	274–331 sh 385	259 sh–269 351–412	278–326 343 sh–390	262 sh–271 348–389	278–303 383
MeOH + NaOAc H_3BO_3	264–377	262–373	254–271 346	272–346	272–336	271–335

Table III. ^{13}C NMR data (in ppm) of the flavone-C-glycosides **Pc 1–Pc 3** from *Plagiomnium cuspidatum* and **Pe 1–Pe 3** from *Plagiomnium elatum* compared with values from literature. The spectra of **Pe 1–Pe 3** were measured at ambient temperature (298 K) while the spectra of **Pc 1–Pc 3** were measured at 373 K (DMSO-d_6, 100 MHz).

Assignments	**Pe 1**	Luteolin [16]	**Pe 2**	Isoorientin [16]	**Pe 3**	Isofurcatain [29]	Lut-7-O-gluc [16]	**Pc 1**	**Pc 2**	**Pc 3**
Aglycone										
C-2	164.3	164.5[a]	163.5[a]	163.5[a]	163.3[a]	164.1[a]	164.6	164.1	163.8	164.0
C-3	104.3	103.3	102.7[b]	102.7[b]	102.6[b]	103.2[b]	103.3	103.0	103.3	103.0
C-4	182.2	182.2	181.7	181.7	181.9	182.0	181.8	181.5	181.6	181.7
C-5	161.2	162.1	160.5	160.5	160.8	158.2	161.1	159.6	159.9	159.6
C-6	98.4	99.2	108.8	108.7	109.1	108.0	99.8	110.7	110.7	110.7
C-7	162.9	164.7[a]	163.1[a]	163.0[a]	162.7[a]	163.8[a]	163.0	161.7	161.9	161.9
C-8	105.6[a]	94.2	93.4	93.4	102.6[b]	95.1	95.0	93.7	93.9	93.8
C-9	156.2	157.9	156.1	156.0	152.8	156.6	156.9	156.0	156.0	156.1
C-10	104.8[a]	104.2	103.3[b]	103.3[b]	102.9[b]	102.8[b]	105.5	105.0	105.0	105.1
C-1′	122.8	122.1	121.4	121.3	121.5	121.3	121.6	121.4	121.3	120.9
C-2′	114.3	113.8	113.3	113.2	113.3	128.7	113.7	113.4	111.1	128.0
C-3′	146.1	146.2	145.6	145.6	145.6	116.2	145.7	145.3	150.8	115.7
C-4′	149.9	150.1	149.5	149.5	149.7	161.4	149.8	149.4	147.9	160.9
C-5′	115.9	116.4	115.9	115.9	116.0	116.2	116.1	115.7	115.8	115.7
C-6′	119.6	119.3	118.4	118.8	118.8	128.7	119.1	118.6	120.3	128.0
$-OCH_3$	–	–	–	–	–	–	–	–	56.1	
C-sugar										
C-1″	73.2	–	73.0	72.9	73.0	–	–	72.6[a]	72.6[a]	72.7[a]
C-2″	71.1	–	70.5[c]	70.4[c]	70.8[c]	–	–	69.8[b]	69.8[b]	69.8[b]
C-3″	79.1	–	78.8	78.8	79.0	–	–	78.8	78.8	78.8
C-4″	71.1	–	70.2[c]	70.1[c]	70.0[c]	–	–	70.3[b]	70.2[b]	70.3[b]
C-5″	82.2	–	81.4	81.3	81.6	–	–	80.6	80.6	80.7
C-6″	61.9	–	61.4	61.3	61.6	–	–	60.8	60.8	60.8
C-1‴	–	–	–	–	77.3	77.3	–	–	–	–
C-2‴	–	–	–	–	75.0[d]	74.5[d]	–	–	–	–
C-3‴	–	–	–	–	74.0[d]	74.3[d]	–	–	–	–
C-4‴	–	–	–	–	72.4[e]	72.2[c]	–	–	–	–
C-5‴	–	–	–	–	71.8[e]	72.0[c]	–	–	–	–
C-6‴	–	–	–	–	19.0	18.3	–	–	–	–
O-sugar										
C-1″	–	–	–	–	–	–	100.4	101.4	101.4	101.4
C-2″	–	–	–	–	–	–	73.3	73.4[a]	73.4[a]	73.4[a]
C-3″	–	–	–	–	–	–	76.6	75.8	75.9	75.9
C-4″	–	–	–	–	–	–	70.0	70.5[b]	70.5[b]	70.6[b]
C-5″	–	–	–	–	–	–	77.3	76.9	77.0	76.9
C-6″	–	–	–	–	–	–	61.0	61.0	61.0	60.8

All assignments, bearing identical superscripts in the same column may be interchanged.

The sugar moieties are configurated as β-D-glucopyranose and α-L-rhamnopyranose by comparing their signals between 18 and 90 ppm in the ^{13}C NMR spectrum [16]. Their linkage to C-6 and C-8 at the aglycone is evident by the significant downfield shifts of these carbon signals compared with those of luteolin (Table III).

Whether the glucose is linked to C-6 or C-8 was decided by the fragmentation in EI mass spectra of the permethyl ethers (Table IV). The fragments $i_h[M^+-175]$ and $i_d[M^+-145]$ indicate the loss of a hexosyl and deoxyhexosyl moiety respectively [17]. As in violanthin [18] the signals h_h, i_h and j_h have higher intensities than the corresponding frag-

Table IV. Mass spectroscopical data of permethylated/perdeuteromethylated C-glycosides from *Plagiomnium elatum* and related compounds.

Derivative	Fragments*		Iso-viol.**/Violanthin			*m/e* (rel. intensity) **Pe 3**		**Pe 4**		**Pe 5**		**Pe 6**	
P M	M^+		(27)	718	(23)	748	(23)	748	(16)	778	(16)	734	(14)
	M^+-14	a_1	(8)	...	(16)	734	(19)	734	(11)	764	(11)	720	(9)
	M^+-15	a_2	(21)	...	(36)	733	(34)	733	(27)	763	(26)	719	(22)
	M^+-17	a_3	(–)	...	(–)	731	(10)	–	–	761	(3)	717	(3)
	M^+-29	b_1	(17)	...	(15)	719	(20)	719	(11)	749	(12)	705	(12)
	M^+-30	b_2	(42)	...	(43)	718	(53)	718	(38)	748	(39)	704	(37)
	M^+-31	b_3	(100)	...	(100)	717	(100)	717	(100)	747	(100)	703	(100)
	M^+-47	c_3	(11)	...	(–)	701	(14)	701	(8)	731	(8)	687	(11)
	M^+-59	g_p	(–)	...	(–)	–	–	–	–	–	–	675	(5)
	M^+-73	g_d	(15)	...	(–)	675	(3)	–	–	–	–	–	–
	M^+-103	g_h	(6)	...	(14)	645	(20)	645	(10)	675	(10)	–	–
	M^+-119	h_p	(–)	...	(–)	–	–	–	–	–	–	615	(18)
	M^+-131	i_p	(–)	...	(–)	–	–	–	–	–	–	603	(13)
	M^+-133	h_d	(18)	...	(7)	615	(9)	615	(5)	645	(6)	601	(5)
	M^+-145	$i_d\, j_p$	(34)	...	(13)	603	(19)	603	(10)	633	(3)	589	(7)
	M^+-159	j_d	(6)	...	(–)	589	(4)	–	–	–	–	–	–
	M^+-161	k_p	(–)	...	(–)	587	(15)	587	(6)	617	(8)	573	(5)
	M^+-163	h_h	(6)	...	(35)	585	(31)	585	(25)	615	(27)	571	(8)
	M^+-175	$i_h\, k_d\, l_p$	(15)	...	(41)	573	(36)	573	(27)	603	(40)	559	(10)
	M^+-189	$j_h\, l_d$	(4)	...	(10)	559	(10)	559	(5)	589	(8)	–	–
	M^+-205	k_h	(2)	...	(7)	543	(10)	543	(5)	573	(8)	529	(4)
	M^+-219	l_h	(3)	...	(3)	529	(5)	–	–	559	(3)	–	–
P D M	M^+					781	(15)	778	(16)				
	M^+-18					763	(31)	760	(28)				
	M^+-34					747	(100)	744	(100)				
	M^+-54					727	(1)	726	(6)				
	M^+-140					640	(2)	638	(2)				
	M^+-151					630	(15)	627	(14)				
	M^+-168					613	(3)	610	(2)				
	M^+-173					608	(26)	605	(23)				
	M^+-184					597	(47)	594	(47)				
	M^+-201					580	(7)	577	(8)				

* Nomenclature of the fragments according to Bouillant *et al.* [17]: $g_{h,d,p}-k_{h,d,p}$ are the main fragments of hexoses $_h$, desoxyhexoses $_d$ and pentoses $_p$ in C-glycosylflavones.

** The values for violanthin (apigenin-6-C-glc-8-C-rha) and isoviolanthin are from [17]: all sugars are pyranoses; D-glucose is β-configurated and rhamnose in α-L-rhamnosyl configuration.

ments h_d, i_d and j_d. Thus the glucose is C-6-linked and to **Pe 3** the structure 6-C-β-D-glucopyranosyl-8-C-α-L-rhamnopyranosyl-luteolin is assigned.

To our knowledge this is a new natural compound [19]. The name Elatin is proposed.

Pe 4 is characterized as a chrysoeriol derivative by its fluorescence and UV spectra (Tables I and II). The compound was identified by EI mass spectrometry (Table IV) of its PM ether. The molecular ion (*m/e* = 748) and fragmentation are identical with **Pe 3** and refer to the same sugar moieties; $[M^+-175]$ and $[M^+-145]$ indicate loss of hexose and rhamnose respectively. The mass spectra of their perdeuteromethyl ethers are identical too. The mass difference between both molecular ions confirms the additional methoxyl group of **Pe 4.**

The intensities of h_h, i_h and j_h are significant higher than those of the fragments h_d, i_d and j_d and confirm C-6 linkage of hexose. Thus **Pe 4** is assigned the structure 6-C-hexosyl-8-C-rhamnosyl-chrysoeriol, which is a new natural compound. The identity of **Pe 5** with Lucenin-2 (6,8-di-C-β-D-

Table V. ^{1}H NMR data of the glycosides **Pe 1–Pe 3** from *Plagiomnium elatum* (298 K) and **Pc 1–Pc 3** from *Plagiomnium cuspidatum* (373 K): δ_H in ppm, DMSO-d_6, 400 MHz.

oton	Pe 1	Pe 2	Pe 3	Pc 1	Pc 2	Pc 3
glycone						
3-H	6.63 s	6.67 s	6.69 s	6.62 s	6.79 s	6.72 s
6-H	6.25 s	–	–			
8-H	–	6.48 s	–	6.87 s	6.93 s	6.89 s
2′-H	7.47 d (J = 2 Hz)	7.40 d (J = 2 Hz)	7.34 d (J = 2 Hz)	7.41 dm (J = 2 Hz)	7.56 dm (J = 2 Hz)	7.88 do (J = 8 Hz)
3′-H	–	–	–			6.95 do (J = 9 Hz)
6′-H	7.52 dd (J = 2; 8 Hz)	7.43 dd (J = 2; 8 Hz)	7.38 dd (J = 2; 8 Hz)	6.94 do (J = 8 Hz)	6.98 do (J = 8 Hz)	6.95 do (J = 9 Hz)
5′-H	6.85 d (J = 8 Hz)	6.89 d (J = 8 Hz)	6.90 d (J = 8 Hz)	7.40 ddom (J = 2; 8 Hz)	7.55 ddom (J = 2; 8 Hz)	7.88 do (J = 8 Hz)
5-OH	13.16 s	~	13.72 s	~	~	~
OCH_3	–	–	–		3.92 s	
igar						
1″-H -glucose)	4.66 d (J = 10 Hz)	4.59 d (J = 10 Hz)	4.60 d (J = 10 Hz)	4.79 d (J = 10 Hz)	4.79 d (J = 10 Hz)	4.77 d (J = 10 Hz)
1‴-H)-glucose)				5.01 d (J = 7 Hz)	5.00 d (J = 7 Hz)	4.99 d (J = 7 Hz)
1‴-H -rhamnose)	–	–	5.23 s (broad)	–	–	–
ha-)−CH_3	–	–	1.28 d (J = 6 Hz)	–	–	–
her sugar otons	3–4	3–4	3–4	3–4	3–4	3–4

glucopyranosyl-luteolin) is obvious by cochromatography with authentic samples and its UV, IR and mass spectra.

The permethylated **Pe 6** has a lower (44 mu) molecular mass than the equivalent derivative of **Pe 5** (Table IV). This corresponds with the loss of a $CHOCH_3$ group. In the mass spectrum the typical hexose and pentose fragments [M^+-131] were observed. Since the intensities of the pentose fragments h_p, i_p and j_p are significant higher than the hexose signals h_h, i_h and j_h the pentose unit is C-6-linked. The relative intensities of the pentosyl fragments M^+-131, M^+-119, M^+-145 confirm the xylopyranosyl structure of this sugar [17]. Thus **Pe 6** is assigned the structure 6-C-xylopyranosyl-8-C-hexopyranosyl-luteolin. The only known 6-C-xylosyl-8-C-hexosyl-luteolin is Lucenin 1 (6-C-β-D-xylopyranosyl-8-C-β-D-glucopyranosyl-luteolin).

By UV spectroscopy of the glycosides **Pc 1, Pc 2** and **Pc 3** (Tables I, II) from *Plagiomnium cuspidatum* their respective aglycones were characterized as luteolin, chrysoeriol and apigenin.

After acid treatment always glucose could be detected by TLC and HPLC [20, 21] but no aglycones. The hydrolysates contained mixtures of mono-C-glycosides which were identified by comparison with authentic samples on TLC as orientin-isoorientin (**Pc 1**) and vitexin-isovitexin (**Pc 3**).

The molecular ions in the FAB mass spectra (negative mode) indicate for all compounds two hexose substituents – **Pc 1:** $[M-H]^-$ = 609, **Pc 2:** $[M-H]^-$ = 623, **Pc 3:** $[M-H]^-$ = 593. UV spectra of the hydrolytic products together with PMR and ^{13}C NMR spectra of the underivatized material (Table III) corroborate for each glycoside the linkage of β-D-glucopyranoses at C-6 and C-7. Thus the following structures were assigned (Fig. 1):

Pc 1: 6-C-β-D-glucopyranosyl-luteolin-7-O-β-D-glucopyranoside (Lutonarin).

Pc 2: 6-C-β-D-glucopyranosyl-chrysoeriol-7-O-β-D-glucopyranoside (Isoscoparin-7-O-glucoside).

Pc 3: 6-C-β-D-glucopyranosyl-apigenin-7-O-β-D-glucopyranoside (Saponarin).

The structure **Pc 1** is described the first time for a moss, while the compound is already known from one liverwort [22] and distributed in the higher plants [19].

Pc 2 was known mainly from *Gentiana* species [19, 23] and now described also for bryophytes.

In spite of former reports saponarin (**Pc 3**) was isolated and their structure fully elucidated by NMR spectroscopy, although the reaction with iodine potassium iodide was negative with fresh and dried plant material as well with the isolated substance.

Besides these C-glycosides from both species small amounts of apigenin-7-O-neohesperidoside

were isolated. Further apigenin- and/or chrysoeriol-O-glycosides may occur in both species as minor compounds. Recently flavone-O-glycosides were also reported from other *Plagiomnium* species [24].

Experimental

Plant material

Air-dried gametophytic material of *Plagiomnium elatum* (B. & S.) T. Kop. *Plagiomnium cuspidatum* (Hedw.) Kop. was used according to the description in [11–13].

Extraction and isolation

The detailed extraction of *P. cuspidatum* is described in [11]. The methanolic extract of *P. elatum* was separated by repeated column and paper chromatography with the solvent systems as listed in Table I. Final purification of the isolated compounds was achieved on Sephadex LH 20 with aqueous MeOH as eluent.

TLC

Spray reagents: NA = Naturstoffreagenz A, according to [25]; BR = Benedikt's Reagenz, according to [26].

UV spectroscopy according to [27].

Mass spectra were recorded by FAB technique (negative and positive mode) on a Finnigan MAT 90 in a glycerol matrix with 4–6 keV Xenon atoms.

FD spectra were recorded on Varian MAT 311 with FD source. Permethyl ether and perdeuteromethyl ether were prepared according to [28].

^{13}C NMR spectroscopy (Bruker AM 400): 100 MHz, DMSO-d_6. – *PMR spectroscopy* (Bruker AM 400): 400 MHz, DMSO-d_6.

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