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FLAVONE C-GLYCOSIDES OF *APOMETZGERIA PUBESCENS*

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Key Word Index—*Apometzgeria pubescens*; Metzgeriales; Hepaticae; flavones; di-C-glycosides of apigenin, tricin, tricetin and tricetin 3′,4′-dimethyl ether.

Abstract—Eleven flavone di-*C*-glycosides, including nine which are new, have been identified in gametophytic material of *Apometzgeria pubescens*. Tricetin 6,8-di-*C*-glucoside and tricin 6-*C*-arabinoside-8-*C*-pentoside are the major compounds. Another identified was ferulylisoschaftoside. The chemotaxonomic relevance of the flavonoid pattern of *Apometzgeria pubescens* is briefly discussed.

INTRODUCTION

In the order Metzgeriales flavonoids seem to be fairly widespread [1–4]; thus from 14 investigated species belonging to 8 families, 11 species of 7 families contained flavonoids. Markham *et al.* [5] initially reported the occurrence of flavone glycosides in Hymenophytaceae and Aneuraceae, and later the existence of flavonoids in Dilaenaceae and Symphyogynaceae [6] as well as in Metzgeriaceae, Blasiaceae and Codoniaceae [1] was also demonstrated. Flavonoids, however, may be absent from the Pelliaceae, [1]. While a detailed flavonoid study on two species of *Hymenophytum* (Hymenophytaceae) has been carried out [7], the flavonoids of Metzgeriaceae have never been investigated. In this paper the flavonoids accumulated by *Apometzgeria pubescens* [8] are reported.

RESULTS

From the extract of 80 g air-dried gametophytic material, 11 flavone glycosides (**1–11**) were isolated by combined CC, PC and PLC. The chromatographic data are given in Table 1, the UV spectral data in Table 2 and the MS data of the permethylated (PM) and perdeuteromethylated (PDM) derivatives are in Table 3. The yields were: **1** (142 mg), **2** (10 mg), **3** (120 mg), **4** (10 mg), **5**+**6** (11 mg), **7** (5 mg), **8** (20 mg), **9** (10 mg), **10** (trace), **11** (15 mg).

1 (*tricetin* 6,8-*di*-C-*glucoside*)

The chromatographic and UV spectral data of this compound closely resemble those of tricetin derivatives found in *Plagiochila* [9]. The identification was confirmed by the MS of the PM and PDM derivatives which exhibited molecular ions at *m/e* 808 (PM) and 847 (PDM) respectively, identical with those of a 6,8-di-C-hexopyranosyltricetin [9]. ^{13}C NMR spectroscopy confirmed the tricetin oxygenation pattern. After acid isomerization no additional spot was observed, indicating 6- and 8-substitution with the same hexose. The periodate–$NaBH_4$ degradation product, glycerol, defines the hexose as pyranose, probably glucose, since $FeCl_3$ degradation yielded only glucose. This is confirmed by the ^{13}C NMR spectrum which exhibits pairs of signals for each pair of glucose carbon atoms. These appear at 81.6, 81.0 (5″, 5‴); 79.0, 78.0 (3″, 3‴); 74.3, 73.7 (1″, 1‴); 72.0, 71.0, 70.6, 69.4 (2″, 2‴, 4″, 4‴); 61.2, 60.4 (6″, 6‴) and are analogous to those previously reported for apigenin 6,8-di-*C*-glucoside [10]. The revised assignments are based on those of Chari *et al.* [11]. From the above data this compound is assigned the structure tricetin 6,8-di-*C*-β-D-glucopyranoside. Co-chromatography with the 6,8-di-C-hexopyranosyltricetin from *Plagiochila aspleniodes* [9] on both cellulose and polyamide TLC (BAW, 40% HOAc, cellulose, 80% MeOH, H_2O–MeCOEt–MeOH–2,4-pentanedione, polyamide) indicates that the latter compound is also tricetin 6,8-di-*C*-β-D-glucopyranoside.

2 (*tricetin* 6-C-*arabinoside*-8-C-*hexoside*)

The chromatographic, spectral (UV, MS) and acid isomerization data suggest that this substance is also a 6,8-di-*C*-glycosyltricetin. However in contrast to **1**, the PM and PDM derivatives show molecular ions at *m/e* 764 (PM) and 800 (PDM). These are 44 (47) mu lower than those of **1**, indicating the loss of a CHOMe ($CHOCD_3$) group and suggesting a *C*-pentosyl-*C*-hexosyl structure for **2**. This is confirmed by the appearance of pentose fragments at $M^+ - 119$, -131, -145 (PM), and $M^+ - 126$, -137, -154 (PDM) [12, 13]. Since the relative intensity of the hexose fragment peaks $M^+ - 175$ (PM) and $M^+ - 184$ (PDM) is lower than the pentose fragment peaks $M^+ - 131$ (PM) and $M^+ - 137$ (PDM), the pentose is considered to be attached to C-6 and the hexose to C-8 [12]. Further, since the relative intensities of $M^+ - 131$ (PM) and

Table 1. Chromatographic data of the flavone

	Compound			
	1	**2**	**3**	**4**
Spot fluorescence (254 and 350 nm)				
UV	deep purple	deep purple	deep purple	deep purple
UV/NH_3	yellow–green	yellow–green	green	green
UV/NA	orange	orange	yellow	yellow
UV/BR	dark	dark	green	green
hR_f values†				
Support: Cellulose				
15% HOAc	22	16	26	27
40% HOAc	44	37	65	61
BAW	11	9	28	20
BAW 27%	22	19	44	37
Support: Polyamide				
80% MeOH	43	31	61	67
H_2O–MeCOEt–MeOH–2,4-pentanedione	55	43	65	65

* Key—**1**, tricetin 6,8-diglucoside; **2**, tricetin 6-arabinoside-8-hexoside; **3**, tricin 6-arabinoside-8-pen-**7**, isoschaftoside; **8**, apigenin 6-arabinoside-8-pentoside; **9**, apometzgerin 6-arabinoside-8-pentoside; **10**, †hR_f values all calculated from 1D TLC of purified compounds.

$M^+ - 137$ (PDM) are higher than $M^+ - 119$ (PM) and $M^+ - 126$ (PDM) and those again higher than $M^+ - 145$ (PM) and $M^+ - 154$ (PDM), it may be concluded [13] that the pentose is arabinose. The occurrence of different sugars at C-6 and C-8 is also evidenced by the results of acid isomerization whereby additional spots were produced. From the above data **2** is assigned the structure tricetin 6-*C*-arabinoside-8-*C*-hexoside.

3–6 (*tricin* 6,8-*di*-C-*glycosides*)

The chromatographic behaviour of these closely related substances differs from that of all other constituents. Whereas the underivatized **3** and **4** could be separated by repeated PC, **5** and **6** could not. The PM and PDM derivatives of all four compounds were however clearly separated. The change to green after fuming with ammonia and the striking green fluores-

Table 2. UV spectral data of the flavone

	Compound			
λ_{max} (nm)	**1**	**2**	**3**	**4**
MeOH	358, 275	356, 274	350, 274	351, 275
NaOMe	416, 282 sh, 264 sh 236 sh‡	426, 274‡	418, 340 sh, 284	424, 340 sh, 282 sh, 264
$AlCl_3$	426, 318 sh, 282, 240 sh	420, 316 sh, 280	390 sh, 370 308 sh, 280	390 sh, 370, 310 sh, 281
$AlCl_3$+HCl	390, 370 310 sh, 281	390, 370, 310 sh, 280	366, 308 sh, 280	364, 310 sh, 281
NaOAc	422, 326 sh, 282 sh, 267	418, 280	424, 284, 266	424, 280, 260
NaOAc+H_3BO_3	437, 270	438, 390 280	420, 346, 278	416 sh, 340, 288 sh, 276

*Impurity in a sample of **9**.
†Peak intensity equal to that of the corresponding MeOH spectrum.
‡Decomposition.

C-glycosides from *Apometzgeria pubescens*

Compound						
5	**6**	**7**	**8**	**9**	**10**	**11**
deep purple green green	deep purple green yellow green	deep purple olive green olive	deep purple olive green olive	deep purple deep purple green weak fluorescence	deep purple deep purple green weak fluorescence	deep purple olive green olive
36	36	34	32	52	62	63
71	71	62	64	81	83	88
25	32	28	32	37	37	56
40	48	43	47	51	46	67
72	72	66	52	63	68	68
74	74	54	41	57	65	38

toside; **4**, tricin 6-arabinoside-8-hexoside; **5**, tricin 6,8-dihexoside; **6**, tricin 6-hexoside-8-pentoside; apometzgerin 6-hexoside-8-pentoside; **11**, ferulylisoschaftoside.

cence in UV after spraying with Benedicts reagent (BR) suggest that the flavones have a single free OH group in the B-ring, probably the 4'-OH. This is supported by the UV absorption data (Table 2) [14].

The acid isomerization of **3** and **4** and of the mixture of **5** and **6** indicates *C*-glycosylation and in all cases resulted in the production of additional spots. The molecular ions for **4** and **6** are at *m/e* 764 (PM) and 794 (PDM) respectively, for **3** at *m/e* 720 (PM) and 747 (PDM) and for **5** at *m/e* 808 (PM) and 841 (PDM). The PM derivative of **5** has the same mass as tricetin 6,8-di-*C*-glucoside, but the PDM derivative differs by 6 mu. This signifies that the aglycone of **5** has two OMe groups. It may thus be concluded that the B-ring is methoxylated at C-3' and C-5'. The MS fragmentation pattern shows only hexose fragments; thus the structure of this compound is tricin 6,8-di-*C*-hexoside. Since acid isomerization could be performed only with a mixture of **5** and **6**, it is not clear whether the hexoses are different or not. The PM derivative of

glycosides of *Apometzgeria pubescens*

Compound				
5+6	**7**	**8**	**9+10***	**11**
351, 274	332, 304 sh, 275	336, 304 sh, 275	331, 276	330, 298 sh, 274
426, 340 sh, 282 sh, 260	401, 329, 283	402, 305, 284	388†, 310 sh, 284	383, 335 sh, 284, 230 sh
394, 374, 300 sh, 281 254	386 sh, 354, 308, 282	386 sh, 354 308, 282	353, 308, 282	383 sh, 340, 305, 280, 230 sh
366, 306 sh, 281, 255 sh	382 sh, 350, 306, 282	384 sh, 350, 307, 282	350, 306, 284	383sh, 340, 305, 280, 230 sh
424, 330 sh 284	402, 336 sh, 316 sh, 283	398, 336 sh, 314 sh, 283	386, 283	385, 333, 280
412 sh, 342, 290 sh, 276	324 sh, 306 sh, 282	410 sh, 350 sh, 320 sh, 310 sh 283	410 sh, 310 sh 284	400, 320, 282

Table 3. MS data for the PM and PDM* derivatives

	Compound				
	1	**2**	**3**	**4**	**5**
M^+	808 (847)	764 (800)	720 (747)	764 (794)	808 (841)
Fragments					Relative intensity (%)
M^+	24 (31)	37 (49)	30 (42)	17 (15)	16 (19)
$M^+ - 15$ (−18)	35 (38)	26 (30)	25 (13)	23 (28)	27 (34)
$M^+ - 31$ (−34)	100 (100)	100 (100)	100 (100)	100 (100)	100 (97)
$M^+ - 47$(−52)	15 (10)	10 (8)	6 (3)	9 (11)	9 (6)
$M^+ - 61$ (−64)	14 (5)	16 (18)	16 (19)	15 (21)	—(16)
$M^+ - 119$ (−126)	—(—)	25 (31)	23 (29)	24 (32)	—(—)
$M^+ - 131$ (−137)	—(—)	29 (78)	33 (58)	27 (60)	—(—)
$M^+ - 145$ (−154)	—(—)	9 (14)	10 (13)	8 (21)	—(—)
$M^+ - 163$ (−173)	33 (43)	8 (12)	—(—)	7 (13)	30 (50)
$M^+ - 175$ (−184)	53 (88)	13 (33)	—(—)	11 (26)	43 (100)
$M^+ - 353$	—	—	—	—	—
$M^+ - 367$	—	—	—	—	—

* PDM-values in parentheses.
Relative intensity 100% above *m/e* 300.

3 differs from **5** by 88 mu which suggests the presence of pentoses instead of hexoses. The fragmentation intensities of the pentoses of this compound are similar to those of **2**, indicating that the C-6 pentose is arabinose. Since acid isomerization was observed **3** is considered to be a tricin 6-*C*-arabinoside-8-*C*-pentoside. **4** and **6** give M^+ ions 44 (PM) and 47 (PDM) higher than those of **3**, indicating replacement of one pentose with a hexose. This is supported by the fragmentation pattern which shows pentose and hexose fragment peaks. The fact that for **4** the relative intensity of $M^+ - 175$ is lower than that of $M^+ - 131$ suggests that the hexose is in the C-8 position. For **6** the opposite is true; thus the hexose is in the C-6 position. The C-6 sugar of **4** also appears to be arabinose because it produces pentose fragments of the same relative intensities as observed for **2** and **3**. Additionally, perdeuteromethylation led to a by-product, the MS of which corresponds to PDM 6-formyl-8-*C*-hexosyltricin (M^+ 639). Corresponding by-products of PM and PDM derivatives of other compounds containing arabinose at C-6 (**2, 3, 7, 8, 9**) could be observed by TLC. These by-products show higher hR_f-values than the PM and PDM derivatives respectively, and their production is thought to confirm the presence of 6-*C*-linked arabinose [13]. **4** is therefore tricin 6-*C*-arabinoside-8-*C*-hexoside and **6** tricin 6-*C*-hexoside-8-*C*-pentoside.

7 *and* 8 (*apigenin* 6,8-*di*-C-*glycosides*)

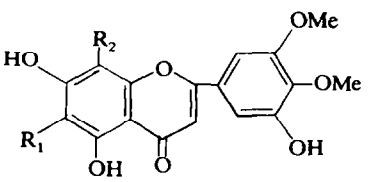
The chromatographic and spectral data and the acid isomerization of these compounds reveal them to be apigenin C-glycosides. The MS of **7** is identical with that of authentic isoschaftoside [13] as also are its chromatographic properties (15% HOAc, 40% HOAc, BAW, TBA, cellulose). **8** (PM) differs by 44 mu from **7** (PM) and gives no hexose fragments. This indicates that the hexose is replaced by a pentose. Again the relative intensities of the different pentose fragments indicate an arabinose moiety at C-6. **8** is therefore an apigenin 6-*C*-arabinoside-8-*C*-pentoside.

9 *and* 10 (*apometzgerin* 6,8-*di*-C-*glycosides*)

As indicated in Table 2, **10** was found as an impurity in **9** and could be separated only as PM and PDM derivatives. **9** and **10** show the same molecular ions and MS fragmentation patterns as **3** and **4**, respectively. The acid isomerization resulted in additional spots but no aglycone was detected. After spraying with BR, the compounds show a weak fluorescence comparable with that of flavonoids with a 3'- or 5'-OH and 4'-OMe. That the 4'-OH is substituted is confirmed by the colour reaction after fuming with ammonia and by the NaOMe shift data (Table 1) [14].

Comparing the MS data for **3** with **9** and **6** with **10**, respectively (Table 3), it is evident that they contain the same number of OMe groups. Since the 4'-position is not free in **9** and **10**, these glycosides must be dimethoxylated in the 3' and 4' (or 4' and 5') positions. To our knowledge this is the first report of this type of aglycone as a natural product. The MS requires that **10** be a hexopentoside and the higher intensity of $M^+ - 175$ (PM) and $M^+ - 184$ (PDM) in comparison with $M^+ - 131$ and $M^+ - 137$ (PDM) suggests a 6-linked hexose. **10** is thus defined as a 6-*C*-hexosyl-8-*C*-pentosyl-3',4'-dimethoxy-5,7,5'-trihydroxyflavone.

9 has a M^+ at *m/e* 720 (PM) and 747 (PDM), respectively, and gives no hexose fragment peaks. From the relative intensities of the pentose fragments it can be concluded again that arabinose is the C-6 sugar. Therefore for **9** the structure 6-*C*-arabinosyl-8-*C*-pentosyl-3',4'-dimethoxy-5,7,5'-trihydroxyflavone is proposed. The trivial name apometzgerin is proposed for the new aglycone 3',4'-dimethoxy-5,7,5'-trihydroxyflavone.



9 R_1 = arabinosyl, R_2 = pentosyl
10 R_1 = hexosyl, R_2 = pentosyl

of the flavone glycosides of *Apometzgeria pubescens*

Compound					
6	**7**	**8**	**9**	**10**	**11**
764 (794)	704 (734)	660 (687)	720 (747)	764 (794)	880
40 (45)	36 (44)	30 (42)	29 (29)	18 (32)	4
29 (33)	22 (27)	28 (25)	21 (27)	24 (29)	20
100 (100)	100 (100)	100 (100)	100 (100)	100 (100)	100
8 (7)	8 (7)	10 (–)	8 (8)	8 (7)	13
2 (–)	15 (19)	16 (16)	14 (20)	1 (–)	18
3 (4)	24 (27)	26 (26)	25 (30)	3 (3)	29
9 (17)	30 (53)	40 (68)	30 (59)	7 (12)	38
2 (2)	9 (13)	14 (14)	9 (14)	3 (2)	22
30 (34)	8 (10)	– (8)	— (—)	26 (26)	—
33 (65)	10 (21)	— (—)	— (—)	32 (46)	—
—	—	—	—	—	29
—	—	—	—	—	24

11 (*ferulylisoschaftoside*)

The chromatographic behaviour of **11** was similar to that of **7** and **8** except that it showed higher hR_f values in most solvents. Alkaline hydrolysis or hydrolysis with lipase liberated ferulic acid, its identity being proved by direct comparison (hR_f, UV, MS) with an authentic sample. The flavonoid moiety (isolated after alkaline hydrolysis) exhibits chromatographic and UV spectral behaviour similar to apigenin glycosides. Acid isomerization, $NaBH_4$ degradation, and MS data were all consistent with this compound being isoschaftoside. This was confirmed by co-chromatography (15% HOAc, 40% HOAc, TBA, BAW, BEW–cellulose) with authentic isoschaftoside. The MS of the PM derivative of **11** shows the M^+ peak at *m/e* 880 which proves the structure to be a monoferulylisoschaftoside. The spectral data require the ferulic acid to be attached to one of the two sugars, and since the fragments of the pentose appear at $M^+ - 119$, -131, -145, and those for the hexose at $M^+ - 353$ and -367, the attachment is most likely to be to the glucose unit. Work on the exact position of the ester linkage is in progress. **11** is therefore apigenin 6-*C*-arabinoside-8-*C*-ferulylglucoside.

DISCUSSION

This is the first detailed study of the flavonoids of a representative of the family Metzgeriaceae. The di-*C*-glycosides of tricetin and its methyl ethers seem to be type compounds of *Apometzgeria pubescens*. Di-*C*-glycosyltricetins had been found previously in *Plagiochila* [9] and more recently in two species of *Takakia* [15], a primitive and isolated genus of liverworts. The flavonoid pattern of *Apometzgeria* consists only of flavone *C*-glycosides and as such is consistent with suggestion that this type of compound might predominate in Metzgeriales [1, 3]. This also appears to be true for Jungermaniales [1], thus clearly distinguishing these orders from Marchantiales in which flavonoid *O*-glucuronides predominate [3]. The available flavonoid data suggest that within the order Metzgeriales, the families Metzgeriaceae and Hymenophytaceae may well be distinguished by their flavonoids. Whereas the characteristic flavonoids of the Metzgeriaceae appear to be flavone *C*-glycosides (Theodor, R., Zinsmeister, H. D., Mues, R., Markham, K. R., unpublished work), the genus *Hymenophytum* has been shown [7] to accumulate, in addition, biosynthetically advanced flavone and flavonol *O*-glycosides. This may indicate that the Hymenophytaceae have diverged from that of other Metzgerialean families.

EXPERIMENTAL

Plant material. Apometzgeria pubescens (Schrank) Kuwah. was collected in August 1977 near Brienz, Bernese Alps, Switzerland. Voucher specimens are deposited in the Herbarium of the Fachrichtung Botanik, Universität des Saarlandes, Saarbrücken.

Extraction and isolation. Air-dried plant material was extracted as described previously [9]. The isolation of the individual compounds was achieved by repeated, combined CC, PC (often 'overrun'!) and PLC. The purified compounds were dried under N_2 (**3, 7, 8**), lyophilized (**2, 11**) or crystallized (**1, 4, 5, 6, 9, 10**). The crystallization, with the exception of **1**, was done from hot MeOH–EtOAc and hot MeOH–H_2O, respectively. **1** precipitated as crystalline powder from aq. MeOH.

Chromatography. CC: Cellulose microcrystalline for CC, Avicel, Merck (solvents: 3% up to 20% HOAc); Sephadex LH20, Roth (solvents: MeOH, 70% MeOH, 80% MeOH). *TLC*: Cellulose microcrystalline for TLC, Avicel, Merck; Cellulose, precoated plastic sheets F 1440, Schleicher u. Schüll (solvents: (a) flavonoids: 15% HOAc, 40% HOAc, *n*-BuOH–HOAc–H_2O 4:1:5, upper phase = BAW, *n*-BuOH–HOAc 27% 1:1 = BAW 27%, BuOH–2-HOAc–H_2O 70:5:25 = BEW, *t*-BuOH–HOAc–H_2O 3:1:1 = TBA; (b) sugars: EtOAc–C_5H_5N–HOAc–H_2O 36:36:7:21; (c) ferulic acid: 6% HOAc, 15% HOAc, BEW, C_6H_6–dioxane–HOAc 90:25:4, 2 N NH_3–*n*-BuOH 1:1, upper phase, H_2O; (d) products of $NaBH_4$ degradation: C_5H_5N–EtOAc–H_2O 2:7:1. Polygram, Polyamide 6, precoated layers, Macherey u. Nagel (for flavonoids solvents: 80% MeOH, H_2O–MeCOEt–MeOH–2,4-pentanedione 13:3:3:1). Si gel 60,

precoated layers, Merck (for PM and PDM derivatives, solvents: $CHCl_3$–EtOAc–Me_2CO 5:1:4 and 5:4:1, respectively). *Preparative TLC and PLC*: Si gel G 60, Merck (for PM and PDM derivatives, solvents: as for TLC, layer 0.25 mm). Cellulose MN 300, Macherey u. Nagel (solvent: BAW, layer 1.5 mm) *PC*: Whatman 3MM (solvent: 15% HOAc; sugars: ETOAc–C_5H_5N–H_2O 12:6:4). Spray reagents: Naturstoffreagenz A (NA) [16], Benedicts reagent (BR) [17], anilinphthalate, Pb (Ac_2)–$Pb(OH)_2$ [18].

Hydrolysis procedures. (a) Alkaline hydrolysis: 1 N KOH, 3 hr, at room temp., acidified with 30% HOAc to pH 5.5 and extracted with Et_2O. (b) Enzymatic hydrolysis: incubation of 2–3 mg of **11** with lipase (pancreas of pig, Serva, Biochemica Heidelberg), pH 5–6 35° for 2 days.

Acid isomerization. 1–2 mg of the compound were treated with 5 ml 2 N HCl at 100° under reflux for 1.5–2 hr.

Periodate–$NaBH_4$ degradation. Performed according to ref. [19].

Ferric chloride degradation. 30 mg of **1** were treated with 300 mg $FeCl_3$ dissolved in 2 ml H_2O and incubated at 100° for 6 hr in a H_2O bath [20].

MS. Preparation of PM and PDM derivatives was performed according to ref. [21].

^{13}C NMR spectroscopy. The spectrum of **1** in DMSO-d_6 was recorded at 30°. Key aromatic carbon signals: 146.7 (C-3′,5′) 138.2 (C-4′) and 121.3 (C-1′) ppm.

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