A Series of Novel Flavanones from Fern Exudates

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The white farinose exudate on the fronds of *Cheilanthes argentea* contains a series of flavanones as minor constituents. These were identified by spectroscopic methods as: 5,4′-diOH,6,7-diOMe flavanone and its 4′-OMe derivative, 5,4′-diOH,7,8-diOMe flavanone and its 4′-OMe derivative, 5,6-diOH,7,8,4′-triOMe flavanone, 5,4′-diOH, 6,7,8-triOMe flavanone and its 4′-OMe derivative. The farina of *Notholaena limitanea* var. *mexicana* contains eriodictyol-7,4′-dimethyl ether and eriodictyol-7,3′, 4′-trimethyl ether as minor components. Both compounds were also identified in the exudate of *N. fendleri,* together with naringenin-7-OMe and naringenin-4′-OMe. In *N. lemmonii* var. *lemmonii* trace amounts of 5-OH,7,3′,4′,5′-tetra-OMe flavanone were detected. Nine of these substances are novel natural flavanones.

Introduction

Farinose Gymnogrammoid ferns are well-known for their production of flavonoids which are deposited externally, especially on the abaxial frond surface [1]. The lipophilic flavonoid aglycones exuded here are mostly methylated flavones and flavonols in the genera *Cheilanthes* Swartz and *Notholaena* R. Br., whereas in *Pityrogramma* Link chalcones and dihydrochalcones are abundant (*cf.* [2]). We recently reported [3] that the conspicuous farinose exudate on fronds of *Pityrogramma pallida* (Weath.) Alt & Grant consists mainly of C-methylated flavanones. Flavanones had been encountered previously only as minor constituents in some cases, probably as cyclisation products of the chalcones present (*cf.* [4]). We now found a number of genuine novel O-methyl flavanones from four farinose ferns. In this paper we report on the structural identification of these compounds.

Materials and Methods

Cheilanthes argentea (Gmel.) Kunze is in cultivation in a greenhouse of the Institut für Botanik der TH at Darmstadt. Fronds of these plants were collected at various times separately. Additional material was supplied by Dr. S. Serizawa, Aichi, Japan (coll. nrs. 26084 and 27798), by Dr. W.-C. Shieh, Taichung, Taiwan, and by Dr. J.-H. Lin, Teipei-Hsien, Taiwan. Also a small quantity of freshly collected fronds were supplied from the Royal Botanic Gardens at Kew (access. nr. 475-64; orig. Peking Botanic Garden). Vouchers are kept at Darmstadt (E. W.).

The fresh or air-dried fronds were rinsed with acetone and toluene to dissolve the farina. Average yield of exudate material is 4–5% of the frond dryweight. The flavonoid patterns of the different collections were not identical; nevertheless the extracts were combined in order to improve the chance of isolating trace constituents. The combined materials were dissolved in boiling benzene and a large amount (more than 90% estimated) of a slightly yellow terpenoid compound crystallized on cooling. This was filtered off and the residue was chromatographed over columns of silica gel (Kieselgel N, Macherey & Nagel, Düren). Further fractionation was done on columns of polyamide (Polyamid SC-6, M & N). In both cases the columns were eluted with toluene and increasing quantities of methylethyl ketone and methanol. This procedure, however, only yielded mixtures of 3–4 flavonoids each with very similar polarity (*cf.* R_f data, Table I). Only one compound could be recovered directly from such a mixed fraction by crystallisation, whereas all others had to be separated by preparative TLC on polyamide (Polyamid DC-11, M & N). Final purifica-

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tion was done by preparative TLC on silica gel with concentrating zone (SilGur 25, UV_{254}, M & N) to yield compounds **1–7**.

Two *Notholaena* species were collected in Mexico by E.-A. Ulrich. *N. lemmonii* var. *lemmonii* D. C. Eaton was collected near Atotonilco/Morelos; *N. limitanea* var. *mexicana* (Maxon) Brown is from near Vizarrón/Querétaro. The major constituents of these ferns' farinas could be crystallized from the crude material. They were identified previously. The remainders were chromatographed each over a small column of silica gel. The fractions thus obtained were further separated by preparative TLC on polyamide. Thus two previously unknown flavanones (**8** and **9**) were isolated from *N. limitanea* and one unknown flavanone (**10**) was isolated from *N. lemmonii* in trace amounts.

From *N. fendleri* Kunze only fragments of the plant were available. These were obtained from the U. S. National Herbarium at Washington, D. C. (Damaree 29438) and from the herbarium of the New York Botanical Garden (Ripley & Barneby 7553). The farina constituents were analysed by direct comparison with reference flavonoids in various TLC systems.

The solvents used for TLC were A) toluene/petrol$_{100-140°}$/methylethyl ketone/methanol 30:90:2:1.5; B) dto, 60:30:10:5; C) toluene/dioxane/MeOH 80:10:10 for polyamide, and D) toluene/methylethyl ketone 9:1 for silica. The reactif used for spraying of chromatograms was "Naturstoffreagens A" (*β*-aminoethyl ester of diphenyl boric acid; C. Roth, Karlsruhe). – Methylation of hesperetin was performed according to [5]. The reaction was stopped after a few minutes by addition of some drops of diluted H_2SO_4. The methyl derivatives were recovered by extraction with ether.

Mass spectra were recorded on a Varian MAT 311 A at the Institut für Organische Chemie der TH Darmstadt. PMR spectra were run on a Brucker HFX 90; ^{13}C-NMR spectra were recorded on a Brucker WH 300 at the Organisch-Chemisches Institut der Universität Heidelberg.

Results

Cheilanthes argentea, compounds **1–7**

The yield of flavonoids finally isolated by the procedures described above was just sufficient for measuring their UV-, MS-, and PMR-spectra. Only the compounds **1**, **2** and **6** were available in amounts sufficient to run a ^{13}C-NMR spectrum. These substances crystallized from ethanol; their melting points were 181 °C (**1**), 146–147 °C (**2**) and 141–142 °C (**6**).

Table I. Chromatographic properties of compounds **1–10**.

Substance	Colour in UV_{366}		$R_f \times 100$ in solvents			
	before spraying "Nat. A"	after spraying "Nat. A"	A	B	C	D
			on polyamide			on silica
1	dark	dark	–	49	73	19
2	dark	dark	56	–	–	41
3	brown	d. reddish-brown	–	55	77	27
4	brown	d. reddish-brown	65	–	–	48
5	dark	brown	(10)	70	92	24
6	dark	dark	–	62	81	23
7	dark	dark	72	–	–	45
8	brownish	greenish-brown	22	75	86	31
9	brownish	greenish-brown	70	–	–	37
10	almost invisible		72	–	–	34

Neither by the spot colour of compounds **1–7** on polyamide viewed in UV_{366} (before and after spraying with "Naturstoffreagens A", *cf.* Table I), nor by their UV-spectra (Table II) the flavonoids could be classified. The mass spectra, however, clearly indicated by M^+ and by characteristic fragments these compounds to be flavanones, all bearing a B-ring with either 1 OH-group or 1 OCH_3-group (Table III). This was readily confirmed by the PMR-spectra (Table IV), exhibiting the AA'BB' spin system typical for a *p*-substituted aromatic ring. The presence of a free OH-group at C-4' in compounds **1** and **3** was shown by the important bathochromic shift in the UV-spectra on addition of NaOEt. The PMR-spectra also showed that none of the compounds was C-methylated. Hence the numbers of OH-groups and OMe-groups present in each substance could be deduced from the relevant M^+ data. In all compounds 1 OH-group can be located at C-5, for the appearance of the relevant signal in the PMR-spectrum indicates that it is hydrogen-bonded. The OMe-groups must occupy positions 7 and 6 or 8 of the molecules. This explains the dark spots in UV_{366} as well as the appearance of absorption peaks at relatively high wave lengths. Flavanones usually have one major maximum in the range of 270–295 nm [6]. Flavones and flavonols with additional

Table II. UV-spectra ($\Delta\lambda_{max}$ nm) of compounds **1**–**10**.

Substance	in EtOH	+ $AlCl_3$	+ NaOEt	+ NaOAc	+ NaOAc + H_3BO_3
1	340, 288	345, 292	383, 286, 242	343, 289	343, 289
2	343, 293	388, 312	365, 291	344, 292	344, 292
3	345, 292	383, 314	380, (287), 248	–	–
4	346, 294	392, 312	368, 290	345, 293	347, 294
5	348, 299	408, 317	342, (258)	344	342
6	369, 285	362, 290	416, (290), 250	362, 286	362, 286
7	365, 293	368, 299	382, dec.	365, 292	365, 290
8	(327), 286	375, 310	(355), 288, (245)	286	290
9	(335), 288	364, 306	–	–	–
10	(325), 287	304	350	–	–

Table III. MS-spectra, *m/e* (rel. int.), 70 eV. MS-fragments are marked according to ref. [19].

Fragment	Substance									
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
M^+	316 (100)	330 (48)	316 (77)	330 (86)	346 (45)	346 (41)	360 (84)	316 (86)	330 (81)	360 (20)
M−1	315 (8)	329 (2)	315 (7)	329 (3)	345 (2)	345 (2)	359 (1)	315 (19)	329 (11)	359 (2)
M−15	301 (10)	315 (7)	301 (7)	315 (8)	331 (2)	331 (3)	345 (4)	–	–	–
Pic F	223 (4)	223 (2)	223 (4)	223 (3)	–	–	–	193 (25)	193 (18)	193 (7)
Pic A + 1	197 (22)	197 (12)	197 (23)	197 (13)	213 (11)	227 (11)	227 (16)	167 (70)	167 (3)	167 (8)
Pic A	196 (92)	196 (100)	196 (100)	196 (100)	212 (100)	226 (100)	226 (100)	–	–	–
A−15	181 (96)	181 (98)	181 (91)	181 (70)	197 (87)	211 (98)	211 (97)	–	–	–
A−28	168 (13)	168 (19)	168 (17)	168 (16)	183 (8)	198 (2)	198 (2)	–	–	–
A−28 −15	153 (13)	153 (41)	153 (39)	153 (45)	169 (17)	183 (42)	183 (40)	–	–	–
Pic B	120 (10)	134 (30)	120 (17)	134 (26)	134 (8)	120 (20)	134 (26)	150 (46)	164 (60)	194 (15)
								137 (100)	151 (100)	181 (44)
B−15	–	–	–	–	–	–	–	135 (32)	149 (22)	179 (14)
				125 (23)		127 (21)				
	91 (9)	91 (34)	91 (18)	91 (23)	91 (12)	91 (21)	91 (30)	–	91 (7)	91 (78)
	69 (18)	69 (40)	69 (30)	69 (34)	69 (15)	69 (55)	69 (46)	–	–	–

Table IV. PMR-spectra of compounds **1**–**7** and **10** (90 MHz, DMSO-d_6/TMS).

	1	**2**	**3**	**4**	**5**	**6**	**7**	**10**
OH−5	11.95 s	11.94 s	11.96 s	12.04 s	12.02 s	11.86 s	11.83 s	12.1 br. sign.
H−6		6.26 s	6.22 s					
H−8	6.25 s			6.22 s				6.10, 6.16
$J_{6/8}$								2.4 Hz
H−2	5.47 dd	5.54 dd	5.47 dd	5.55 dd	5.48 dd	5.50 dd	5.61 dd	5.53 dd
J_{AX}	3.5 Hz	3.5 Hz	3.5 Hz	3.5 Hz	3.5 Hz	3.4 Hz	3.5 Hz	3.0 Hz
J_{BX}	13.0 Hz	12.0 Hz	13.0 Hz	12.5 Hz	12.0 Hz	12.4 Hz	12.0 Hz	13.0 Hz
H−3a/3b	2.74, 3.17	2.75, 3.27	2.75, 3.20	2.80, 3.37	2.75, 3.27	2.80, 3.35	2.88, 3.33	2.78, 3.35
J_{AB}	17.0 Hz	17.0 Hz	17.0 Hz	17.0 Hz	17.0 Hz	17.0 Hz	17.0 Hz	17.0 Hz
$-OCH_3$	3.66	3.78	3.65	3.58	3.61	3.77	3.37	3.68 (1 OCH_3)
	3.83	3.80	3.85	3.75	3.66	3.84	3.77	3.80 (3 OCH_3)
		3.85		3.83	3.75	3.97	3.84	
							4.03	
H−2′,6′	7.30 AA′	7.47	7.32	7.44	7.44	7.34	7.51	6.87
H−3′,5′	6.78 BB′	6.95	6.84	6.97	6.97	6.85	7.06	
OH−4′	9.58 br. sign.					9.61 br. sign.		
					(OH−6 exchanged)			

Table V. ^{13}C-chemical shifts of compounds **1**, **2**, and **6**.

Carbons	Flavanone		
	1	**2**	**6**
2	78.87	78.54	78.82
3	42.20	42.10	42.52
4	197.59	197.34	198.44
5	160.7 [a]	160.64 [a]	157.94 [a]
6	128.28	129.68	133.50 [b]
7	157.87 [a]	158.47 [a]	154.98 [a]
8	92.17	92.04	132.96 [b]
9	154.18	154.07	150.96
10	102.67	102.53	104.11
1′	128.85	130.45	128.89
2′/6′	128.37	128.19	128.31
3′/5′	115.28	113.84	115.37
4′	158.67 [a]	159.49 [a]	150.96 [a]
OCH_3	56.37	55.12	61.06
	60.15	58.24	61.23
		59.89	

Signals marked with [a] or [b] within any column may be interchanged.

substituents at C-6 and/or C-8 are well-known as "yellow flavonoids", *i.e.* exhibiting higher absorption maxima. In **6** and **7** even the crystalline substances are light yellow, whereas flavanones normally are colourless. These compounds must be substituted at C-6 and at C-8 according to their MS fragmentation.

So far the results were corroborated by the ^{13}C-NMR-spectra (Table V) of compounds **1**, **2** and **6**. ^{1}H-NMR-spectra and ^{13}C-NMR-spectra did not allow, however, to decide whether the two OMe-groups at the A-ring of compounds **1**–**4** are located either at C-6 and C-7 or at C-7 and C-8. The differences between the relevant signals are not significant. In the case of **1** and **3** our decision is based on the characteristic reactions with $AlCl_3$. While this results in a bathochromic shift of 38 nm in **3**, there is almost no reaction in **1**. Compounds **6** and **7**, which must have OMe-groups at C-6, also show no significant reactions. This observation is interpreted as a consequence of steric hindrance of complex-forming with OH at C-5 in compounds **1**, **6** and **7**. The corresponding pair of isomeric C-methyl flavanones, strobopinin (5,7-diOH,6-CH_3) and cryptostrobin (5,7-diOH,8-CH_3), shows the same properties [3]. Hence the free proton at ring A is assigned to C-8 in **1** and to C-6 in **3**.

Unfortunatelly it is not possible with the $AlCl_3$-reaction to discriminate between **2** and **4** in the same way: both compounds show bathochromic shifts of 19 (**2**) and 14 (**4**) nm immediately after addition of $AlCl_3$, which increase to 45 (**2**) and 46 (**4**) nm after a few minutes. Because of the identical brown spot colour of compounds **3** and **4** we suggest that the free proton is assigned to C-6 in **4** and to C-8 in **2**. This is supported by the difference in spot colour between strobopinin (dark) and cryptostrobin (brown) [3]. The same colour behaviour also has been observed by other workers (J. Favre-Bonvin, pers. comm.). – The second OH-group in **5** must be located at C-6 because of the important bathochromic shift with $AlCl_3$.

The flavanones **1**–**7** thus have the structural formulas shown in Fig. 1. We admit that there remains a small uncertainty as to the exact substitution of ring A in compounds **1**–**4**, but it is hoped that the structures proposed here will be affirmed by synthesis of these substances.

Notholaena species, compounds **8**–**10**

In *N. limitanea* var. *mexicana* the major farina constituent is 2′,6′-diOH,4′-OMe dihydrochalcone [2]. The following flavonoids were identified as minor constituents by comparison with authentic samples on polyamide and on silica: apigenin-7-OMe, ap-4′-OMe, and ap-7,4′-diOMe; galangin-3,7-diOMe; kaempferol-3,7-diOMe and kae-3,7,4′-tri-OMe; quercetin-3,7,4′-triOMe and qu-3,7,3′,4′-tetra-

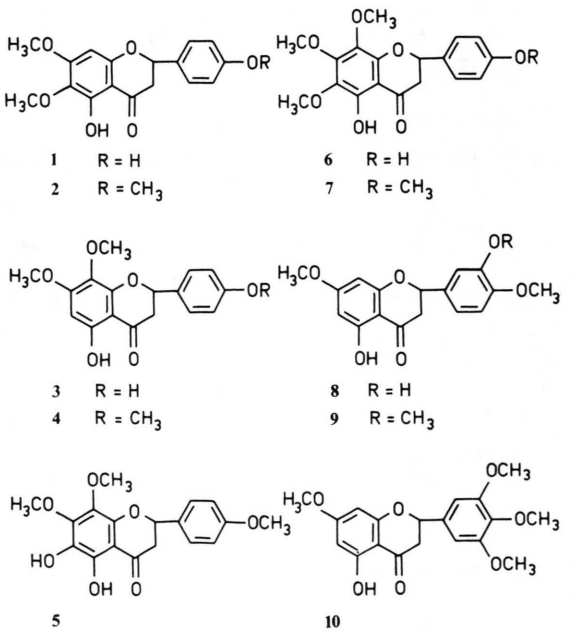

Fig. 1

OMe; pinocembrin, naringenin-7-OMe. In addition two spots were observed behaving like flavanones, but not identical with any of the reference compounds available. These substances could be isolated as white crystals from EtOH, m. p. 160 °C (**8**) and 156 °C (**9**). Based on observations on their TLC behaviour the compounds were tentatively identified. The spot with lower R_f (**8**) appeared on polyamide as the third member of a R_f-graduation pinocembrin – naringenin-7-OMe – **8**; the R_f-step from nar-7-OMe to **8** parallels the step from naringenin to hesperetin (eriodictyol-4′-OMe). The compound with higher R_f is the third member in the sequence pinocembrin-7-OMe – naringenin-7,4′-diOMe – **9** on silica. Hence it was assumed that both might be methyl derivatives of eriodictyol, the homologues flavanone after pinocembrin and naringenin. Comparison with the reaction products of partial methylation of hesperetin supported this assumption by yielding two major reaction products which were chromatographically identical with the two original compounds. These could be confirmed by their spectral data (*cf.* Tables II and III) as eriodictyol-7,4′-diOMe and eriodictyol-7,3′,4′-triOMe. The melting point of comp. **8** agrees with data from literature (163–164 °C, [7]) and confirms the discrimination from the isomeric eriodictyol-7,3′-diOMe (m. p. 149 °C, [8]).

In *N. lemmonii* var. *lemmonii* the farina is composed mainly of a dihydrostilbene, called notholaenic acid [9]. One major constituent could be identified by direct comparison as naringenin-7-OMe. In addition a very minute amount could be isolated of a component that on TLC behaved much like eriodictyol-7,3′,4′-triOMe, but was not identical with this flavanone. Its M^+ indicated that it was a flavanone with 1 OH- and 4 OMe-groups. The PMR data revealed its structure as 5-OH, 7,3′,4′,5′-tetraOMe flavanone, which is in accordance with the UV-spectra and with its MS fragmentation.

N. fendleri obviously is a very rare representative of this genus; only fragments of fronds could be obtained from herbarium specimens. These were sufficient, however, to allow the identification of some of the farina constituents by direct chromatographic comparison. Two minor constituents could be identified as eriodictyol-7,4′-diOMe (**8**) and eriodictyol-7,3′,4′-triOMe (**9**). Naringenin-4′-OMe is present in larger amounts, whereas only traces of naringenin-7-OMe could be detected.

Discussion

As has been mentioned in the introduction, flavones hitherto have been encountered only scarcely in fern farina. There is only one report on C-methyl flavanones forming the farina on *Pityrogramma pallida* [3]. With the asiatic fern *Cheilantes argentea* we now know another species in which the farina flavonoid pattern is characterised by the presence of flavanones. In this fern, however, the bulk of the exudate consists of an unknown terpenoid (analysis is under way). Seven flavanones could be isolated and identified so far. Two or three further minor constituents, probably flavones or flavonols, are under further investigation. The distribution of all these flavonoids in the various collections and specimens at our diposal will be discussed elsewhere.

The seven flavanones described here from *Cheilanthes argentea* are all novel compounds. They are closely related structurally. The substances **1** and **2** are methyl ethers of carthamidin (5,6,7,4′-tetraOH flavanone, [10]); substances **3** and **4** are methyl ethers of isocarthamidin (5,7,8,4′-tetraOH flavanone, [10]). Both tetrahydroxy flavanones had been obtained by hydrolysis of carthamin, a chalcone glycoside of the flowers of safflower (*Carthamus tinctorius*) [11]. Only the 5,6,7-triOMe derivative of carthamin has been found as natural product. It was isolated together with the corresponding chalcone from aerial parts of *Eupatorium odoratum* [12]. – The completely substituted A-ring as found in compounds **5**–**7** is known from two flavanones, namely isopedicin (6-OH,5,7,8-triOMe) and didymocarpin (7-OH,5,6,8-triOMe) from the leaf exudate of *Didymocarpus pedicellatus* [13, 14] as well as from kanugin (5,6,7,8-tetraOMe) from fruits of *Lindera erythroxylon* [15] and of *Popowia cauliflora* [16]. In the latter compounds, however, the B-ring is unsubstituted. – Natural flavanones with five substituents have not been known previously.

Compounds **8** and **9** from *Notholaena limitanea* var. *mexicana* are methyl derivatives of eriodictyol. Two dimethyl ethers of this flavanone are known to date, the 7,3′-diOMe and the 7,4′-diOMe derivative. The latter, which is identical with compound **8**, has been isolated as a natural product only from bark of *Prunus persica* and called persicogenin [7]. Compound **9**, the 7,3′,4′-trimethyl ether of eriodictyol, is a novel compound.

Compound **10** from *Notholaena lemmonii* var. *lemmonii* has five substituents. In this case the B-ring is tri-O-substituted. 3′,4′,5′-substitution for flavanones is known hitherto only once, from 5-OH,6,7,3′,4′,5′-pentaOMe flavanone, that has been found recently as a glycoside in aerial parts of *Sideritis mugronensis* [17]. It may be mentioned that the latter is the only known flavanone with 6 substituents. Compound **10** also is a new natural flavanone.

Pinocembrin, naringenin-7-OMe (sakuranetin) and naringenin-4′-OMe (isosakuranetin) are flavanones found in various plants. This is the first time, however, that they have been identified as genuine constituents of fern farina.

The nine novel flavanones presented in this report remarkably increase the number of known natural flavanones. As far as we know less than 50 existed hitherto, 41 of which may occur as free aglycones (*cf.* [18]).

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