New Frond Exudate Flavonoids from Cheilanthoid Ferns

Eckhard Wollenweber

Institut für Botanik der Technischen Hochschule, Schnittspahnstraße 3, D-6100 Darmstadt, Bundesrepublik Deutschland

James N. Roitman

Western Regional Research Laboratory, USDA-ARS, 800 Buchanan Street, Albany, C.A. 94710, U.S.A.

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Cheilanthes argentea, Notholaena spp., *Pityrogramma triangularis, Platyzoma microphylla,* Pteridaceae

A series of new flavonoid aglycones have been identified in the frond exudates of the fern *Cheilanthes argentea,* in five species of *Notholaena,* in *Pityrogramma triangularis,* and in *Platyzoma microphylla.* These aglycones comprise several rare flavonoids and five novel natural products: 5,7,8-trihydroxy-3-methoxy-6-methyl flavone, 3,5,2′-trihydroxy-7,8,4′-trimethoxy flavone, 5,2′-dihydroxy-3,7,8-trimethoxy flavone, 5,7,4′-trihydroxy-2′-methoxy flavanone, and 3,5,4′-trihydroxy-6,7,8-trimethoxy flavone. The novel flavonoids were characterized by their NMR spectral data.

Introduction

The farinose frond exudate of the Asiatic fern *Cheilanthes argentea* has been shown previously to be comprised of several rare flavanones [1] and two diterpene acids [2]. In the earlier study, several minor constituents, suspected to be flavones and flavonols, remained unidentified, due to paucity of material and lack of markers. Eight flavonoids have now been isolated in at least minute amounts, allowing reliable identification by direct comparison with authentic samples that had become available in the meantime. One product was identified by spectroscopic studies and found to be a new natural flavone. The situation was similar in several other cheilanthoid ferns, from which four rare flavonoids were identified by direct comparison with markers, and four novel natural products where identified by NMR spectroscopic studies. These results, which considerably increase the number of known fern frond exudate flavonoids, are described in the following report.

Materials and Methods

Cheilanthes argentea was collected in August, 1979 near Lu Shan, Taiwan, by J.-H. Lin (Teipei-Hsien). *Notholaena californica* was collected in December, 1981 south of Bumblebee near Interstate 17 in Yavapai Co., A.Z. and at Salt River Canyon on Hwy 60 in Gila Co., A.Z., respectively, by E. Wollenweber and G. Yatskievych (vouchers of the latter collection, E. Wollenweber & G. Yatskievych 81-489, are kept in ARIZ and in E.W.'s private herbarium in Darmstadt). *Notholaena dealbata* was collected in Travis Co., Texas (D. Seigler, No. 1033: near West Cave, along Pedernales River, 29-12-68, and No. 1035: on bluffs over the Colorado River at Miller Dam, 08-01-69). Only fragments of herbarium specimens were available for *Notholaena delicatula* (Pringle 2581 from Edo. Jalisco, Mexico; voucher kept in N.Y.) and for *Notholaena ekmanii* (Ekman 6004, Ekman 10011 and U.S. 1040117, all from Cuba; vouchers in U.S.). *Notholaena lemmonii* was collected 11 miles S.W. of Mazocahui on Sonora Highway 21 between Moctezuma and Hermosillo, Edo. Sonora, Mexico (voucher E. Wollenweber and G. Yatskievych 81-503 in ARIZ and in Darmstadt). Bulk material of *Platyzoma microphyllum* came from Nicotine Creek, S.W. of Mareeba, Queensland, Australia (voucher R. & A. Tryon 7342 at G.H. and in Darmstadt). *Pityrogramma triangularis* var. *triangularis* was collected at School Land Gulch near the Pardee Reservoir, C.A. in July, 1980 (voucher EW-3 at Darmstadt). Fragments of a herbarium specimen in Dale M. Smith's collection, designated as "chalcone type" (Smith 43223, 5/19/78) and a fragment of a herbarium specimen kept at U.S. (S. C. Mason, 20 Jan. 1911, collected near Banner, San Diego Co., C.A.) were also used.

Reprint requests to E. Wollenweber.

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Exudate material was obtained as usual by briefly rinsing the fern fronds with acetone. Further treatment of bulk portions was reported earlier for *Cheilanthes argentea* [1], *Notholaena californica* [3], *N. lemmonii* [4] and *Platyzoma microphyllum* [5]. The minor products now analyzed were isolated from remainders of earlier studies by preparative TLC on silica (solvents: A, toluene–methylethyl ketone 9:1 and B, toluene–dioxane–glacial acetic acid 18:5:1). Comparison with authentic flavonoids was performed on polyamide DC-11 (solvents: C, toluene–petrol$_{100-140}$–methylethyl ketone–MeOH 12:6:2:1, D, toluene–dioxane–MeOH 8:1:1, and E, toluene–methylethyl ketone–MeOH 12:5:3) and on silica (solvents A and B). Chromatograms were viewed in UV_{366} before and after spraying with Naturstoffreagenz A (NA; 0.5% in MeOH). All flavonoid markers were available in E. W.'s laboratory.

Mass spectra were recorded on a Varian MAT 311 at 70 eV by direct inlet. ^1H and ^{13}C NMR spectra were recorded in DMSO-d_6 on a Nicolet NT-WB 200 FT spectrometer at 200 and at 50 MHz, respectively.

Results and Discussion

From the residual material of our earlier study on the farinose frond exudate of *Cheilanthes argentea*, several trace constituents were isolated, partly by preparative TLC. Small amounts and lack of purity precluded reliable spectroscopic studies, and therefore these flavonoids could only be identified when relevant markers had become available. They were then identified unambiguously by direct comparison with authentic flavonoid markers in several solvent systems on both polyamide and silica. They were thus found to be scutellarein-6,7-dimethyl ether (cirsimaritin), herbacetin-7-methyl ether, herbacetin-7,8-dimethyl ether, herbacetin-7,8,4′-trimethyl ether (tambulin), 6-hydroxy-kaempferol-6,7,4′-trimethyl ether (mikanin), 5,7,4′-trihydroxy-6,8-dimethoxy flavone (desmethoxy-sudachitin), 5,7-dihydroxy-6,8,4′-trimethoxy flavone (xanthomicrol) and 5,4′-dihydroxy-6,7,8-trimethoxy flavone (nevadensin). Cirsimaritin, herbacetin-7,8-dimethyl ether, desmethoxy-sudachitin, xanthomicrol and nevadensin were then confirmed by major peaks in their mass spectra. It was fortunate that the one product that did not match any marker (compd. **1**), could be isolated in an amount sufficient to obtain both ^1H NMR and ^{13}C NMR spectra (Tables I, II). On polyamide TLC it appears as a brownish spot at R_f 0.29 (solv. C) that turns dark ochre on spraying with NA. MS fragmentation (Table I) indicated that it was a flavone or a flavonol with three hydroxy and three methoxy groups (M^+ 360), methoxylated at C-8 or at both C-8 and C-6 ($M^+ - 15 < M^+$). It turned out to be an isomer of a flavonol previously isolated from *Gutierreza microcephala* (5,7,4′-trihydroxy-3,6,8-trimethoxy flavone = sarothrin; compd. **11** in ref. [5]), which facilitated interpretation of its NMR data (see Tables I and II). The positions of the B ring signals in the ^{13}C NMR spectrum of **1** agreed exactly with those values reported [6] for the B ring of kaempferol, and the A ring signals were in good agreement with those reported for 5,4′-dihydroxy-3,6,7,8,3′-pentamethoxy flavone (compd. **1** in ref. [5]) after minor adjustments are made for having 3-OH instead of 3-OMe. This is in accordance with UV spectral data (Table I). Flavone **1** is thus 3,5,4′-trihydroxy-6,7,8-trimethoxy flavone, a new natural product.

A screening of some 17 herbarium specimens of *Cheilanthes argentea* revealed that small amounts of compd. **1** are present in plants from Taiwan and traces were observed in plants from Japan, whereas it appears to be lacking in those from the Asiatic mainland. The other flavonoids reported above might also be restricted to plants from Taiwan and from Japan, but this is hard to tell from thin layer chromatographic comparison of fern fragments for these trace constituents. At any rate this observation requires further studies and needs to be considered with regard to our earlier observation on the occurrence of the 3 *R*-hydroxy derivative of *E*-13-labdadien-15-oic acid in plants from Taiwan only [2]. The flavones and flavonols now reported are related structurally to the prevailing flavanones [1] insofar as all of those exhibit O-methylation at positions 6 and/or 8.

A small amount of compound **2** was isolated from *Notholaena californica*. It appears on polyamide TLC as a dark spot (R_f 0.95, solvent C) that remains dark on spraying with NA. Its mass spectrum suggested it to be a flavone or a flavonol with two hydroxy and three methoxy groups (M^+ 344). In addition to three OMe signals and a low field chelated 5-OH signal, the ^1H NMR spectrum of **2**

Table I. ^{1}H NMR, MS and UV data of compounds **1, 2, 4, 5,** and **6.**

	Compound **1**	Compound **2**	Compound **4**	Compound **5**	Compound **6**
^{1}H NMR δ [ppm]					
H-2			5.64, dd, J = 3, 13 Hz; 1 H		
H-3$_{ax}$			3.34, dd, J = 13, 17 Hz; 1 H		
H-3$_{equ}$			2.64, dd, J = 3, 17 Hz; 1 H		
H-6		6.62, s; 1 H	6.08, *d, J = 2 Hz; 1 H	6.53, s; 1 H	
H-8			6.10, *d, J = 2 Hz; 1 H		
H-3′			6.36, d, J = 2 Hz; 1 H	6.42, d, J = 2 Hz; 1 H	
H-5′			6.28, dd, J = 2, 8.5 Hz; 1 H	6.48, dd, J = 2.8 Hz; 1 H	
H-6′			7.22, d, J = 8.5 Hz; 1 H	7.44, 4, J = 8 Hz; 1 H	
H-2′/6′	8.08, d, J = 8.8 Hz; 2 H				8.16, m; 2 H
H-3′/4′/5′					7.60, m; 3 H
H-3′/5′	6.96, d, J = 8.8 Hz; 2 H	6.98, four line m; 2 H			
H-4′/6′		7.40, three line m; 2 H			
OMe	4.02, 3.90, 3.83, s; 3 × 3 H	3.91, 3.713, 3.708, s; 3 × 3 H	3.80, s; 3 H	4.04, 3.90, 3.88, s; 3 × 3 H	3.82, s; 3 H
5-OH	12, 30, s; 1 H	12.46, br s; 1 H	12.14, br s; 1 H	12.67, s; 1 H	12.35, s; 1 H
OH	10.22, 9.84, s; 2 × 1 H		9.6, br s; 2 H		
6-Me					2.05, s; 3 H
MS m/z (rel. int.)	360 (M^+, 88), 345 (M−15, 100), 317 (M−43, 26), 302 (9), 284 (6), 259 (5), 180 (5), 147 (9), 121 (32)	344 (M^+, 100), 329 (M−15, 88), 300 (45), 181 (93), 153 (79)	302 (M^+, 35), 284 (M−18, 95), 193 (8), 180 (7), 167 (100)	360 (M^+, 100), 345 (51), 329 (14), 317 (55), 272 (11), 167 (45), 149 (47), 129 (13)	314 (M^+, 100), 313 (75), 271 (28), 182 (21), 105 (57), 77 (75)
UV λ^{EtOH} [nm]					
MeOH	379, 240, 277, 258	348 (303), 264	325 sh, 287	394, 270	(340), 284
$AlCl_3$	435, 373, 270	410, 325 sh, 276	375, 307	435, 307, 270	365 sh, 305
+HCl	436, 373, 270	406, 315 sh, 274	372, 307	432, 355, 303	(350), 290
NaOH	437, 258	370, 261	450, 325, 284	398, 270	(340), 277
NaOAc	–	–	–	405, 270	295
+H_3BO_3				406, 271	300

(Table I) revealed an aromatic singlet (H-6) and two non-first order multiplets (2 H each). Assuming oxygenation at 2′, a computer simulation of the signals of the four contiguous B ring protons was performed using the following shift and coupling parameters: J_{ortho} = 8 Hz; J_{meta} = 1 Hz; J_{para} = 0; line width 0.69 Hz; d 7.00 (H 3′); d 7.38 (H 4′); d 6.95 (H 5′); d 7.40 (H 6′). This resulted in a very good approximation of the shapes of the two observed multiplets. The ^{13}C NMR spectrum of **2** (Table II) supports the location of the single B ring oxygen on C 2′ for the following reason: the C 1′ signal appeared in the region for aromatic carbons shifted upfield by *ortho* or *para* oxygen, and since the B ring is clearly not symmetrically substituted, C 4−O is excluded. Comparison of the A ring resonances of **2** with those of herbacetin 7,8,4′-trimethyl ether [7] shows very good agreement, and the C 2 and C 3 resonances show that a 3-OMe is present. Hence the structure of **2** is: 5,2′-dihydroxy-3,7,8-trimethoxy flavone, to the best of our knowledge a new natural flavonol (*cf.* [8]). The relevant 7-methyl flavonol has been found, as its natural 8-acetate, in the frond exudate of *Notholaena sulphurea* [9], while a dihydroflavonol with the same O-substitution (3,5,2′-trihydroxy-7,8-dimethoxy flavanone, 2′-acetate) has been found earlier in the frond exudate of *Notholaena neglecta* [10]. The two

Table II. ^{13}C NMR data of compounds **1–6.**

Carbon	Compd. **1**	Compd. **2**	Compd. **4**	Compd. **5**	Compd. **6**	Carbon	Compd. **3**
						1	125.8
2	152.1	155.3	74.0	149.1	154.8	2	130.6
3	135.9	138.6	41.1	137.9	138.6	3	116.0
4	176.5	178.1	197.5	177.1	178.4	4	160.1*
5	147.5	156.2#	163.4#	156.0	150.8	5	116.0
6	135.0	95.4	94.5	94.6	107.0	6	130.6
7	147.8	157.8#	167.3	157.0	152.7		
8	132.5	127.9	93.7	128.0	123.9		
9	144.2	148.2	163.2#	148.2	143.5		
10	105.6	104.6	102.5	104.0	103.5		
1′	121.6	117.1	115.1	111.8	130.5	1′	106.2
2′	129.6	156.9#	158.7	159.1	128.5#	2′	165.3#
3′	115.6	115.9	102.4	102.0	128.7#	3′	91.0
4′	159.5	131.7	155.8	161.9	131.0	4′	165.6#
5′	115.6	118.4	106.4	104.7	128.7#	5′	93.9
6′	129.6	130.1	128.4	130.4	128.5#	6″	161.8*
3-OMe	–	60.1	–	–	60.0	α	123.7
6-OMe	60.6	–	–	–	–	β	143.4
7-OMe	61.8	56.6	–	56.3	–	C=0	192.2
8-OMe	61.5	60.9	–	60.8	–	OMe	56.1, 55.6
2′-OMe	–	–	55.9	–	–		
4′-OMe	–	–	–	55.0	–		
6-Me	–	–	–	–	7.9		

#, *: Values in any vertical column may be interchanged.

previously reported major frond exudate flavonols of *N. californica* also exhibit 8- and 2′-O-substitution, and so do the two major flavonols from *N. aliena* [3].

Compound **3,** isolated from *Notholaena dealbata,* forms a dark spot (R_f 0.51 on polyamide, solvent C) that with NA turns ochre with a dark margin. MS fragments at *m/z* 207 and 181 indicated a chalcone with OH-substituted B ring and the NMR spectra (Table II) showed it to be 4,6′-dihydroxy-2′,4′-dimethoxy chalcone (flavokawin C). The assignments of the NMR signals were aided by comparison with the spectra of the known 4-methyl ether (synthetic sample provided by L. Jurd). This rare flavonoid is reported here for the first time as constituent of a fern exudate.

Compound **4** comes from *Notholaena lemmonii.* It was crystallized from dilute acetic acid, m.p. 203 °C (dec.). It forms a gray spot on polyamide (R_f 0.45 in solvent D) that turns dull yellow with NA. Its UV spectra and the base peak, in the MS, at *m/z* 167 point to a flavanone structure; an important peak at M-18 further indicates 2′-OMe substitution (*cf.* Table I). The ^1H NMR spectrum of **4** showed couplings and chemical shifts for three non-aromatic (H 2 and H 3) signals typical for dihydroflavones. In addition signals were observed for a chelated hydroxyl at low field (5-OH), a single methoxyl, a pair of *meta* coupled A ring protons, and three B ring protons one of which showed both *ortho* and *meta* coupling coupling to protons not coupled to one another. This coupling pattern indicates that the B ring is substituted 2′,4′, 2′,5′, or 3′,4′.

Comparison of the ^{13}C spectrum of **4** (Table II) with that of eriodictyol [6] shows that with the exception of the C 2 signal all of the A and C ring resonances are the same and thus **4** is hydroxylated at C 5 and C 7. However, the B ring signals of **4** were very different from those of eriodictyol and rule out 3′,4′-oxygenation. Furthermore the C–O signals both appear far enough downfield to eliminate the possibility that these carbons are *ortho* or *para* to one another, and hence **4** has 2′,4′-oxygenation. The decision to assign the single methoxyl to C 2′ rather than C 4′ was made after comparing the observed B ring resonances with estimated chemical shifts for the two possible methyl ethers of 4-(*n*-propyl)-resorcinol. [These values were calculated from the reported chemical shifts for 4-(*n*-propyl)-

resorcinol [11] and the shift perturbations caused by methylation of B ring hydroxyls observed in the spectra of a series of flavonols from *Gutierrezia microcephala* (Table III in ref. [5]).] Because the calculated values for four of the B ring resonances are very similar for both isomers, the decision was based on the values for C 1′ and C 5′. (The calculated values were respectively 116.0 and 107.8 for C 1′ and C 5′ of the 2′-OMe isomer and 121.1 and 102.7 for the 4′-OMe isomer; the observed values for **4** were 115.2 and 106.4.) Compound **4** is thus 5,7,4′-trihydroxy-2′-methoxy flavanone.

Compound **5** was also isolated from *Notholaena lemmonii* as yellow crystals, m.p. 272–273 °C (EtOH). It shows a dull olive-green spot on polyamide TLC (R_f 0.28 in solvent D) which turns dull yellow or ochre with NA. In the MS the molecular ion (M^+ = 360.0856) was the base peak and provided the formula $C_{18}H_{16}O_8$ consistent with a trihydroxy-trimethoxy flavone. Significant peaks were observed (Table I) at *m/z* 345 (M^+–Me, 51%), 329 (M^+–OMe, 14%), suggesting 2′-oxygenation, and 317 (M^+–COMe, 55%). The ^{1}H NMR spectrum of **5** revealed signals for a chelated OH at low field (5-OH), three methoxyls, and the aromatic region of the spectrum showed a one H *ortho* doublet and a three H multiplet about 1 ppm farther upfield, which on closer examination proved to be comprised of a singlet, a *meta* doublet, and a double doublet. The singlet was assigned to a lone A ring proton and the coupled signals to three B ring protons. The B ring substitution pattern was determined after studying the ^{13}C NMR spectrum (Table II).

The A and C ring resonances in the ^{13}C spectrum suggested that **5** is an 8-oxygenated flavonol and the chemical shifts matched those of the A and C ring signals of tambulin (herbacetin 7,8,4′-trimethyl ether) whose spectrum we had determined earlier. The chemical shifts of the two oxygenated carbons on the B ring indicated, as in the case of compound **4,** that the oxygens were neither *ortho* nor *para* to one another and were thus attached to C 2′ and C 4′. In a manner analogous to that used to locate the single B ring methoxyl of **4** estimates of shift values for 2′-OH/4′-OMe and 2′-OMe/4′-OH based on reported values for morin [6] were made and compared with the observed values for **5.** Again only the C 1′ and C 5′ signals allowed a distinction to be made between the two possible isomers. Estimated shifts for C 1′ and C 5′ respectively of the 2′-methyl ether of morin (107.6 and 107.8) and for the corresponding 4′-methyl ether (112.7 and 105.6) were compared with the observed resonances (111.8 and 104.7) in the spectrum of **5** suggesting that **5** is a 4′-methyl ether. The structure of **5** is thus 3,5,2′-trihydroxy-7,8,4′-trimethoxy flavone. The absence of a significant bathochromic shift of band I in the UV spectrum (Table I) of **5** upon addition of NaOMe (4 nm observed) lends further support to the conclusion that a 4′-OH is not present.

Compound **6** is a minor frond exudate constituent in a particular chemotype of *Pityrogramma triangularis*. Its colour reaction on spraying with NA (dark spot becomes bluish-violet in daylight; R_f 0.32 in solvent C) is characteristic for a flavone or flavonol with 5,7,8-trihydroxy substitution. M^+ 314 suggested two hydroxy and two methoxy groups, but its polarity on TLC indicated that it had three hydroxy groups instead, and hence we suspected the presence of a C-methyl group. This was confirmed by the NMR data of this product. The ^{1}H spectrum (Table I) revealed signals for a chelated hydroxyl at low field (5-OH), a C-methyl signal, a methoxy resonance and two complex multiplets integrating for five protons in the aromatic region. The ^{13}C spectrum (Table II) had B ring signals which exactly matched those of galangin [6] confirming an unsubstituted B ring for **6.** Comparison of the A and C ring resonances with those of a number of 5,7,8-trihydroxy-3-methoxy flavones [5] showed that, with the exception of the C 6 signal, agreement was very close. Placing the remaining substituent (the C-methyl group) at C 6 explains the downfield shift of that carbon and shows that **6** is 5,7,8-trihydroxy-3-methoxy-6-C-methyl flavone, a novel natural C-methyl flavonol. It has the same O-substitution pattern as pityrogrammin (compound **2** in [12]) and two further flavonols (compounds **11** and **12** in [13]), reported earlier for *P. triangularis*.

In another specimen of *P. triangularis,* 8-hydroxygalangin was suspected due to the same bluish-violet colour reaction with NA in daylight, and its presence was confirmed by comparison with an authentic sample.

Spots with intense light yellow fluorescence (UV_{366}) had been observed in at least two *Notholaena* species and in *Platyzoma*. We have now been

able to show, by direct comparison with markers, that galangin-5-methyl ether is present in the frond exudate of *Notholaena delicatula, Notholaena ekmanii,* and *Platyzoma microphyllum* (*cf.* ref. [14]). *N. ekmanii* also produces galangin-5,7-dimethyl ether. Both of these 5-methyl flavonols, appear as conspicuous TLC spots, but are present as trace constituents only. Galangin-5-methyl ether has so far been reported only in the bud exudate of poplar species and the derived bee hive product propolis. It has been observed in the bud exudates of *Populus candicans, P. deltoides, P. euramericana, P. jackii* and some hybrids [15]. Galangin-5,7-dimethyl ether has so far been reported only once, namely from a certain population of *Pityrogramma triangularis* var. *triangularis* (compd. **EW-2** in ref. [16]).

The rather rare flavonoids and especially the novel ones reported in the present paper illustrate once more the high capacity of cheilanthoid ferns to synthesize a diverse variety of flavonoid aglycones. We assume that those "farinose" species which have not yet been analyzed in detail due to lack of material would further extend the array of known flavonoids. Unfortunately some of these plant species are so rare that it is unlikely they ever will be abundant enough to permit isolation of sufficient material for thorough characterization, but perhaps some will be identified in the future by comparison with markers, when such become available, either by synthesis or from other plant sources.

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