Rare Flavonoids from *Odixia* and *Ozothamnus* spp. (Asteraceae, Gnaphalieae)

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Representatives of the genera *Odixia* and *Ozothamnus*, Australian Asteraceae belonging to the tribe Gnaphalieae, have been analyzed for the presence of flavonoid aglycones accumulated on leaf and stem surfaces. Fiftytwo more or less lipophilic flavonoids have been identified. Methyl ethers of apigenin, luteolin, kaempferol and quercetin are abundant, while rare methyl ethers of isoscutellarein, 8-hydroxy galangin, herbacetin and gossypetin appear to be characteristic. The distribution of rare flavonoids is discussed.

Introduction

The genus *Odixia* houses only two species, native to Australia. They both form "shrubs with sessile, decurrent, glandular-hairy leaves" (Bremer, 1994). The genus *Ozothamnus* comprises some 50 species, native to Australia, New Zealand and New Caledonia. They form "shrubs with sessile, linear, ligulate or spatulate, or minute and scutelliform, often xeromorphic or almost fleshy leaves, often hairy and glandular-hairy" (Bremer, 1994). In the course of extensive systematic studies on Gnaphalieae (Puttock, in prep.) and phytochemical studies on the occurrence of exudate flavonoids (Wollenweber, 1990; 1996), we have now analyzed the two *Odixia* species as well as a series of *Ozothamnus* species for externally accumulated flavonoid aglycones. In the present paper we report the results with ten species that have been found to produce more or less rare flavonoid aglycones. Those exhibiting only trivial methylated flavones and flavonols will be included and considered later in a chemotaxonomic survey, when further species have been analyzed.

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Material and Methods

About ten branches per species, ca 0.3 m long each, were collected (including inflorescences when available) in the field or from field vouchered specimens propagated from cuttings in the Australian National Botanical Garden, Canberra. The fresh leaf and inflorescence material was stripped from the twigs, weighed and dried in a oven at 50 °C for 30 hours. The amounts of dry material used in this study varied between 2 g (*Ozothamnus expansifolius*) and 114 g (*Oz. hookeri*). The average amount of exudate recovered was 13.4% of the dry weight (4.5% in *Oz. ferrugineus*, 33.9% in *Oz. ledifolius*). Voucher specimens of original field collections and of on-propagated materials are kept at the Australian National Herbarium (CANB) and others.

Collection data and provenances are as follows:

Odixia achleana (P.Morris) Orchard: Kellevie, Hospital Ck Reserve, Franklins rd, Tasmania, 42° 45'S 147° 50'E, 26. Jan 1989, *Davies 1265, Ollerenshaw & Burns* (AD, CANB, HO, MEL).

Od. angusta (N. A.Wakef.) Orchard: Kellevie, Hospital Ck Reserve, Franklins rd, Tasmania, 42° 45'S 147° 49'E, 26. Jan 1989, *Davies 1266, Ollerenshaw & Burns* (AD, CANB, HO, MEL).

Oz. ericifolius Hook. f.: 2.2 km S of Interlaken along Dennistoun rd to Bothwell, Tasmania, 42° 10'S 147° 07'E, 16. Jan 1989, *Davies 921, Ollerenshaw* (AD, CANB, MEL, PERTH).

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Oz. ericifolius: near Remarkable Cave, Tasmania, 43°11' 147° 50', 27. Dec 1995, *Buchanan 14045 & Puttock* (CANB).

Oz. expansifolius (Sieber ex P. Morris et J. H. Willis) A.Anderb.: Pencil Pine Creek, Cradle Mountain-Lake St Clair National Park, 41° 35' 30„S 145° 57'E, 25. Apr 1988, *Burns 29(CANB).*

Oz. hookeri Sond.: Snowy Flats, Mt Gingera, ACT, 35° 33'S 148° 46'E, 6.x.1995, *Puttock 1061 & Telford* (CANB). Oct 95.

O. hookeri: Big Bend, Mt Wellington, Tasmania, 42° 53'S 147° 13'E, 28. Dec 1995, *Puttock 1302* (CANB).

Oz. ledifolius (DC.) Hook. f.: Big Bend, Mt Wellington, Tasmania, 42° 53'S 147° 13'E, 28. Dec 1995, *Puttock 1301* (CANB).

Oz. ledifolius: between The Springs and Chalet, Tasmania, 42° 54'S 147° 14'E, 28. Dec 1995, *Puttock 1305* (CANB).

(Showing identical composition, the exudates of these two collections were combined prior to analysis).

Oz. lycopodioides Hook. f.: Tasman Hwy at Black Bridge Gully, c.5 km WSW of Orford, Tasmania, 42° 34'S 147° 49'E, 26. Jan 1989, *Davies 1259, Ollerenshaw & Burns* (AD, CANB, HO).

O. obcordatus DC.: Tunnel Hill, Hobart,Tasmania, 42° 52'S 147° 25'E, 29. Feb 1995, *Puttock 1306* (CANB).

Oz. purpurescens DC.: Tunnel Hill, Hobart, Tasmania, 42° 52'S 147° 25'E, 29. Dec 1995, *Puttock 1307* (CANB).

Oz. scutellifolius Hook. f.: summit of Mt Brown, Port Arthur, Tasmania, 43° 12' 147° 52', 27. Dec 1995, *Buchanan 14040 & Puttock* (CANB).

Air-dried plant material was briefly rinsed with acetone to dissolve the lipophilic exudate. Concentrated solutions were defatted, passed over Sephadex LH-20, and subjected to column chromatography on silica and/or polyamide SC-6 as previously reported (Wollenweber *et al.*, 1996). Fractions were monitored and comparisons with markers were made by TLC on polyamide DC-11 with the solvents (v/v) petrol$_{100-140}$ – toluene – methylethyl ketone – methanol 12:6:1:1, toluene – petrol$_{100-140}$ – MeCOEt – methanol 12:6:2:1, toluene – dioxane-methanol 8:1:1 and toluene – methylethylketone – methanol 12:5:3 and on silica with the solvents toluene – methylethylketone 9:1 and toluene – dioxane – glacial acetic acid 18:5:1. Chromatograms were viewed under UV_{366} before and after spraying with Naturstoffreagenz A (NA). Terpenoids were visualized by spraying silica plates with $MnCl_2$ reagent, followed by heating (Jork *et al.*, 1989). Several products were isolated by preparative TLC on silica. Herbacetin-3,7-diMe was finally purified by prep. HPLC on a 10 µm Econosil RP-18 column with a linear solvent gradient from 45% to 95% MeOH in 1% aq. HCO_2H over 50 min. at 5 ml min^{-1}. The UV trace was recorded at 280 nm. Unless otherwise stated, flavonoid identifactions were made by direct comparisons on TLC and in some cases confirmed by UV-spectra and by EI (70 eV) mass spectra. Several structures were elucidated by NMR spectroscopy. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ at 200 MHz and 50 MHz, respectively. The ^1H-^{13}C HMBC experiment with herbacetin-3,7-diMe was performed using a standard pulse sequence. Spectral widths of 13 and 210 ppm were used in the H (600 MHz) and C (150.9 MHz) dimensions, respectively. Melting points are uncorrected.

Results

Flavonoid identification

All species studied exhibit resinous exudates which mostly consist of terpenoids. Our interest, however, is in the occurence of more or less lipophilic flavonoid aglycones which are dissolved in this resin. The results of flavonoid identification in 2 species of *Odixia* and 10 species of *Ozothamnus* are presented in Table I. Abbreviations OH = hydroxy group and Me = methyl ether are used throughout, in the table as well as in the text. In the following we want to comment and substantiate some of the flavonoid identifications.

The UV-, MS- and ^1H-NMR spectra of isoscutellarein and iscoscut-4'-Me, isolated from the two *Odixia* species; agreed with previously reported data (Jay and Gonnet, 1973; Horie *et al.*, 1983). Their thus far unpublished ^{13}C-NMR data are presented in Table II. *Odixia achlaena* as well as *O. angusta* exhibit several minor TLC spots. Their colour reaction (bluish-violet in daylight after spraying with NA) indicates 5,7,8-triOH-substitution for these components, too (Wollenweber and Roitman, 1991; Wollenweber *et al.*, 1994).

Ozothamnus hookeri (coll. Puttock 1061; no. 6 in Table I) yielded Herbacetin-3,7-diMe as the ma-

Table I. 1 = *Odixia achlaena*, 2 = *Od. angusta*, 3 = *Ozothamnus ericifolius* (Davies 921), 4 = *O. ericifolius* (Buchanan 14045 & Puttock), 5 = *O. expansifolius*, 6 = *O. hookeri* (Puttock 1061 & Telford), 7 = *O. hookeri* (Puttock 1302), 8 = *O. ledifolius*, 9 = *O. lycopodioides*, 10 = *O. obcordatus*, 11 = *O. purpurescens*, 12 = *O. scutellifolius*.

Species	1	2	3	4	5	6	7	8	9	10	11	12
Flavonols												
Galangin			×	×	×	×		×			×	
Gal-3-Me			××	××	×	×					×	
Gal-7-Me								×				
8-OH-Gal								×				
8-OH-Gal-8-Me					×							
8-OH-Gal-3-Me			×					×				×
8-OH-Gal-7-Me								×				
8-OH-Gal-3,8-Me			×								×	
8-OH-Gal-7,8-Me								×				
8-OH-Gal-3,7,8-Me					×	×						
Kaempferol			×		××	×	×	×			×	×
Kae-3-Me				×	×	×				×	×	×
Kae-7-Me					×							×
Kae-4′-Me												×
Kae-3,7-Me					×	×	×			×		×
Kae-3,4′-M										×		×
Kae-7,4′-Me												×
Kae-3,7,4′-Me												×
Herbacetin						×						
Herb-3-Me						×	×					×
Herb-8-Me					××	×						
Herb-3,7-Me						×	×					
Herb-3,8-Me						×				×	×	
Herb-7,8-diMe					×					×		
Herb-3,7,8-triMe					×	××				×		
Herb-3,8,4′-triMe										××		
Herb-7,8,4′-triMe					×					×		
Herb-3,7,8,4′-tetra					×	××			×	××		
Quercetin			×		×	×		×			×	×
Qu-3-Me			×	×					×		×	
Qu-7-Me					×							×
Qu-3′-Me			×		×						×	
Qu-3,7-Me									×			×
Qu-7,3′-Me												
Qu-3,7,4′-Me												×
Quercetag-3,6-Me									×			
Gossyp-3,7,8-Me									×			
Goss-3,7,8,3′,4′-Me									×			
Flavones												
Apigenin	×				×	×						×
Ap-7-Me												×
Ap-4′-Me												×
Ap-7,4′-Me												×
Isoscutellarein	×	×										×
Isoscut-4′-Me	×	×										×
Luteolin												
Lut-4′-Me												×
Flavanones/Flavanonol												
Pinocembrin				×				×			×	
Pinoc-7-Me						×		××				
Eriodictyol								×				
Pinobanksin				×							×	
Chalcones												
2′,4′,6′-OH-chalcone								×				
2′,6′-OH-4′-OMe-chalcone								×				

jor component. It forms fine yellow needles, mp 274°. UV and MS are in accordance with literature data (Sakakibara *et al.*, 1975). ^{1}H NMR δ ppm (d_6-DMSO): 12.21 (s, 5-OH), 10.28 (s, 4'-OH), 8.82 (s, 8-OH), 8.03 (d, J = 8,8 Hz; H-2'/H-6'), 6.97 (d, J = 8.8 Hz; H-3'/H-5'), 6.57 (s, H-6), 3.91 (s, 7-OMe), 3.80 (s; 3-OMe). ^{13}C-NMR see Table II. The structure was confirmed by ^{1}H-^{13}C heteronuclear multiple bond correlation (HMBC) spectroscopy. The OH-5 proton signal (12.21 ppm) provided a good starting point for the assignement of the A-ring resonances; it showed correlations with C-5, C-6 and C-10. The aromatic A-ring proton was located at C-6 since the hydroxy proton resonating at 8.82 ppm correlated with C-7, C-8 and C-9, and was thus assigned to OH-8. The location of the aromatic A-ring proton at C-6 was further corroborated by cross peaks between H-6 and carbons 5,7, 8, and 10. Carbon-7 interacted with the methoxy protons resonating at 56.4 ppm, from wich a 7-OMe followed. The other methoxy function was located at C-3 likewise. Finally, a free 4'-OH followed from correlations observed for the OH-4'-signal at 10.28 ppm with C-3',5'and C-4'.

8-OH-Gal-3,7,8-triMe was isolated from the exudate of *Ozothamnus hookeri* (coll. Puttock 1302; no. 7 in Table I). Its UV and MS data agree with those reported (Urzua and Cuadro, 1989a). The structure was confirmed by ^{1}H NMR δ ppm (d6-DMSO): 12.38 (s, 5-OH), 8.04 (m, H-2'/H-6'), 7.62 (m, H-3'/H-4'/H-5'), 6.62 (s, H-6), 3.93, 3.83, 3.81 (s, 3-OMe, 7-OMe, 8-OMe) (Urzua and Cuadro, 1989a, used $CDCl_3$). For ^{13}C-NMR data see Table II.

Ozothamnus ledifolius is exceptional in that it exhibits two chalcones: 2',4',6'-trihydroxychalcone and 2',6'-dihydroxy-4'-methoxychalcone (corresponding to pinocembrin and pinoc-7-Me). The methoxy chalcone and pinocembrin-7-methyl ether are the major constituents. It can not be excluded that at least part of the flavanone was formed from the corresponding chalcone by cyclisation of ring C during work-up.

8-OH-Gal-7-Me forms yellow needles, mp 238–240° (Lit. 246°). The UV and MS data agree with those previously reported (Wollenweber *et al.*, 1978).

8-OH-Gal-7,8-diMe was obtained as yellow crystals, mp 200–202° (Lit. 202–203°; Ferraro *et al.*, 1985). Its UV and MS data agree with those

Table II. ^{13}C NMR data of some rare 8-O-substituted flavones and flavonols.

Carbon No.	8-OH-Galangin-7,8-diMe	8-OH-Galangin-3,7,8-triMe	Herbacetin-3,7-diMe	Gossypetin-3,7,8-triMe	Isoscutellar.	Isoscut-4'-Me
1	146.2	155.5	155.8	155.8	163.5	163.1
3	137.2	138.8	137.4	137.6	103.2	103.0
4	176.8	178.6	178.4	178.3	182.1	182.1
5	156.0	156.4	152.7	156.3	153.0	153.1
6	95.4	95.9	95.4	95.7	98.6	98.7
7	158.1	158.4	154.0	158.1	153.4	153.5
8	128.4	128.4	126.1	128.4	125.0	125.0
9	148.0	148.1	143.7	147.8	145.5	145.5
10	103.6	104.7	104.4	104.4	103.3	103.3
1'	131.1	130.1	120.8	120.9	121.4	123.1
2'	127.5	128.1	130.3	115.3	128.6	128.4
3'	128.7	128.8	115.6	145.3	115.8	114.5
4'	130.2	131.2	160.2	148.9	161.1	162.3
5'	128.7	128.8	115.6	115.9	115.8	114.4
6'	127.5	128.1	130.3	120.7	128.6	128.4
3-OMe	–	60.0	59.6	59.6	–	–
6-OMe	–	–	–	–	–	–
7-OMe	56.6	56.6	56.4	56.5	–	–
8-OMe	61.1	61.1	–	61.1	–	–
3'-OMe	–	–	–	–	–	–
4'-OMe	–	–	–	–	–	55.5

previously reported, while the ^1H-NMR data are somewhat different (Ferraro *et al.*, 1985); they are, therefore, given here. ^1H NMR δ ppm (d6-DMSO):12.18 (s, 5-OH), 9.79 (s, 3-OH), 8.19 (m, H-2'/H-6'), 7.59 (m, H-3'/H-4'/H-5'), 6.61 (s, H-6), 3.93, 3.83 (s, 7-OMe/8-OMe). ^{13}C-NMR see Table II.

Gossypetin-3,7,8-triMe was isolated from *Ozothamnus lycopodioides* as yellow crystals, mp 242–243°. Its UV and MS spectra were consistent with the established structure and with literature data (Henrick and Jefferies, 1965). ^1H-NMR δ ppm (d6-DMSO): 12.51 (s, 5-OH), 9.78 (s, OH), 9.52 (s, OH), 7.60 (d, J = 2 Hz; H-2'), 7.51 (dd, J = 2,8 Hz; H-6'), 6.93 (d, J = 8 Hz; H-5'), 6.58 (s, H-6), 3.91, 3.82, 3.80 (s, 3 x OMe). ^{13}C-NMR see Table II.

One of the diterpene constituents forming the exudate of *Ozothamnus hookeri* (coll. Puttock 1302; no. 7 in Table I) was obtained in crystalline form. Analysis of its NMR spectrum revealed it to be the well known (-)-*ent*-16α-kauranol (Hugel *et al.*, 1965). Its NMR data agree with those reported in literature (Patra *et al.*, 1980; Hanson *et al.*, 1976). The same diterpene was also crystallized from the resin of *Ozothamnus scutellifolius*.

Flavonoid distribution.

In the following the distribution of 8-methoxy-flavonoids is discussed for really rare compounds, i. e. such that have previously been found in nature not more than three times.

Isoscutellarein and its 4'-methyl ether (takakin) are rare flavones. To our knowledge they were found here for the first time as free aglycones. A previous finding of free isoscutellarein in *Pinguicula* laves (Jay and Gonnet, 1973) was probably due to hydrolysis during extremely long extraction).

8-OH-Gal-3-Me also is a rare flavonol. It has previously been reported only from *Achyrocline flaccida* (Norbedo *et al.*, 1984) and *Gnaphalium robustum* (Urzua and Cuadra, 1989a); in the resinous exudate of the latter it is also present in esterified form (Urzua and Cuadra, 1989b). 8-OH-gal-7-Me was thus far found only as its natural acetate and butyrate, in the farinose frond exudate of *Notholaena* species (Wollenweber *et al.*, 1978; Wollenweber and Yatskievych, 1982). 8-OH-Gal-8-Me was previously reported from leaf resin of *Adenostoma sparsifolium* (Proksch *et al.*, 1982), from bud exudate of *Platanus acerifolia* (Kaouadji and Ravanal, 1988) and from leaf resin of *Nothofagus antarctica* (Wollenweber *et al.*, 1988). 8-OH-Gal-7,8-

diMe was found as a natural flavonoid only once before, in *Achyrocline tomentosa* (Ferraro *et al.*, 1985). 8-OH-Gal-3,7,8-triMe (methylgnaphaliin) was found for the first time in aerial parts of *Gnaphalium obtusifolium* (Hänsel and Ohlendorf, 1969), later in *Achyrocline bogotensis* (Torrenegra *et al.*, 1982) and in *Gnaphalium robustum* (Urzua and Cuadra, 1989a).

Herbacetin-3-Me was so far only known from the resinous exudate of *Gutierrezia microcephala* (Roitman and James, 1985). Herbacetin-8-Me (sexangularetin) was found as an aglycone *in flower heads of Eupatorium gracile (Torrenegra et al.*, 1984) and in the leaf resin of Enceliopsis nudicaulis (Proksch *et al.*, 1987). Herbacetin-3,7-diMe was first reported from the leaf resin of *Larrea tridentata* (Sakakibara *et al.*, 1975) Later it was erroneously described as a constituent of *Pluchea odorata* (Arriaga-Giner *et al.*, 1983). The *Pluchea* component, however, is the 6,7-dimethyl derivative of 6-hydroxykaempferol (eupalitin; Wollenweber and Arriaga, 1983, unpublished). Our finding thus is only the second report of this flavonol as a natural product. Herbacetin-7,8-diMe was thus far found only twice as an aglycone, namely in flower heads of *Eupatorium gracile* (Torrenegra *et al.*, 1984) and in the farinose frond exudate of the fern *Cheilanthes argentea* (Wollenweber and Roitman, 1991). Herbacetin-3,7,8-triMe was known as an exudate constitutent from *Larrea tridentata* (Zygophyllaceae) (Bernhard and Thiele, 1981) and from *Cleome spinosa* (Wollenweber and Dörr, 1992). Plant sources for further relatively rare methyl derivatives of 8-hydroxygalangin, herbacetin, and gossypetin are found in (Wollenweber, 1988) and (Wollenweber, 1994).

Our analysis of *Odixia* and *Ozothamnus* exudate flavonoids has revealed the presence of numerous flavonoid aglycones in these lipophilic materials. The presence of 8-O-substituted flavones and flavonols is a characteristic feature in many species. In *Oz. ericifolius* as well as in *Oz. hookeri* the flavonoid patterns of the two collections each differ remarkably. They thus seem to represent two different chemotypes. Further studies on this subject are required, therefore, also in the other species. Additional species of *Ozothamnus* and also of the closely related genus *Cassinia* are presently being analyzed. The chemotaxonomic implications of our results will be discussed in a later paper.

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