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FLAVONOIDS IN LEAVES AND INFLORESCENCES OF AUSTRALIAN CYPERACEAE

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Key Word Index—Cyperaceae; flavonoids; aurones; sulphuretin; tricin; luteolin 7-methyl ether; flavonol methyl ethers; chemotaxonomy.

Abstract—A survey of 170 Australian species of Cyperaceae belonging to 35 genera has confirmed that this family has a highly characteristic flavonoid pattern in leaf and inflorescence. Aurone pigments, the most distinctive family constituents, were found in the leaves of 25 % of the sample and in the inflorescences of 40 %. Sulphuretin was found for the first time in the family, in *Carex appressa*. Flavones, such as tricin and luteolin, are very common; in addition, a variety of methyl ethers were detected. Luteolin 5-methyl ether was found in further genera, while luteolin 7-methyl ether, diosmetin and acacetin were detected for the first time in the Cyperaceae. Flavonols and their methyl ethers occurred in over one-third of the species, particularly in the leaves, being especially well represented in the genera *Fuirena*, *Gahnia*, *Lepidosperma* and *Mesomelaena*. Myricetin was found only twice, in two *Baumea* species. The 3-desoxyanthocyanidin carexidin was found in the inflorescences of eight species, i.e. in 5 % of the sample. Taxonomically, the results are mainly of interest at the generic and specific level, where the patterns sometimes show useful correlations with morphology. At the tribal level, the Sclerieae are the most distinctive, with higher than average frequency of flavone *C*-glycosides, flavonols, proanthocyanidins and aurones, and lower than average frequency of flavones.

INTRODUCTION

Previous surveys of flavonoids in the Cyperaceae have shown that this monocotyledonous group has a distinctive pattern of constituents in leaf, fruit and inflorescence [1–4]. Flavones, *C*-glycosylflavones, flavonols, proanthocyanidins, 3-desoxyanthocyanidins and aurones are all represented, as are a number of rarer derivatives, such as 6-hydroxyluteolin, luteolin 5-methyl ether, 7,3′,4′-trihydroxyflavone, and various kaempferol and quercetin methyl ethers [3, 4]. The correlations of flavonoid patterns with geography [3], systematics [5] and anatomy [6] are of interest in this cosmopolitan family.

The Cyperaceae is particularly well represented in the Australian flora and, in a recent paper, we described the results of surveying the flavonoids in 92 species of *Cyperus*, the type genus of the family [4]. Significant correlations were observed between flavonoid frequencies and sub-generic groupings, while a number of constituents novel to the family were encountered. The present paper is an extension of that survey to a representative sample of other genera in the Australian Cyperaceae. Additionally, it was hoped to apply the results to taxonomic studies in the family, the chemical characters being of particular interest in a group that is often difficult to classify on morphological characters alone.

RESULTS

General

The detailed results of surveying leaf and inflorescence (including fruit, when present) of some 170 species of Cyperaceae are shown in Tables 1 and 2. Flavonoids were identified by standard procedures in direct and hydrolysed extracts. Of the samples surveyed 11 are in *Cyperus*, the remainder belonging to 35 other genera. This represents the widest flavonoid survey so far attempted within the sedges, with coverage of nearly half the known genera.

The frequency of flavonoid occurrences within and outside of *Cyperus* are compared in Table 3, the data from within *Cyperus* being drawn from our earlier paper [4]. As will be seen, the pattern is not very different although not unexpectedly, many more compounds are found outside *Cyperus* than within it. In the present discussion, the major flavonoid types will be considered in turn.

Flavones

The present survey shows that the two flavones luteolin and tricin, occurring as *O*-glycosides, are the major flavonoids in the leaf not only in *Cyperus* but throughout the Cyperaceae. In the case of the inflorescences, luteolin is very common but tricin less so (Table 2). A major difference between *Cyperus* and the other genera is the relative infrequency of flavone *C*-glycosides in *Cyperus* compared with their regular occurrence (in 48 % of the sample) in the family as a whole (Table 1). The nature of the *C*-glycosylflavones present has not been determined, but from R_f data they appear to be of the usual type. In fact, iso-orientin has been obtained from leaves of northern temperate *Carex* species [2] and of the tropical *Rhynchospora eximia* [3]. Also, a variety of apigenin and chrysoeriol (luteolin 3′-methyl ether) *C*-glycosides have been characterized in stems of *Trichophorum cespitosum*, a

Table 1. The distribution of flavonoid aglycones in leaves of some Australian Cyperaceae

Sub-family, tribe,* genus and species	Flavone C-glycosides	Flavones	Flavonols	Proantho-cyanidins	Aurones	Collector's name, No. and State of collection
CYPEROIDEAE						
Hypolytreae						
Hypolytrum nemorum (Vahl) Spreng.	–	–	–	–	–	Hind 2712, Q.
Exocarya sclerioides (F. Muell.) Benth.	–	Tr	–	Cy	Au	Wilson 4498, N.S.W.
Lepironia articulata (Retz.) Domin	+	Lu	Qu3ME	–	Au	Wilson 3919, N.S.W.
Chorizandra cymbaria R. Br.	+	Lu	–	Cy	–	Wilson 4387, N.S.W.
C. sphaerocephala R. Br.	+	Lu	–	Cy	–	Wilson 4386, N.S.W.
Chrysitrix distigmatosa C. B. Clarke	+	Lu, Lu7Me	–	–	–	Wilson 2615, W.A.
Rhynchosporeae						
Schoenus apogon R. and S. }	–	Tr	–	Cy, Pg	–	Wilson 4309, N.S.W.
S. apogon R. and S. }	–	Tr	Qu	Cy, Pg	–	Wilson 4328, N.S.W.
S. apogon R. and S. }	–	Tr	–	Cy	–	Wilson 4395, N.S.W.
S. asperocarpus F. Muell.	–	Tr, Lu	–	–	Au	Haegi 1958, W.A.
S. bifidus (Nees) Boeck.	+	Lu	Qu	–	–	Wilson 3040, W.A.
S. brevifolius R. Br.	–	Tr, Lu	–	Cy, Dp	–	Wilson 3930, N.S.W.
Schoenus sp. aff. *brevisetis*	+	Tr	Flavonol methyl ethers	–	Au	Wilson 2935, W.A.
S. calostachyus (R. Br.) Poir	–	Tr	–	Cy	Au	Wilson 3693, Q.
S. clandestinus S. T. Blake	+	Tr, Lu	Qu	–	–	Wilson 2710, W.A.
S. curvifolius (R. Br.) Poir	+	–	–	–	Au	Wilson 2800, W.A.
S. ericetorum R. Br.†	–	Lu	–	(Cy)	Au	Coveny 11356, N.S.W.
S. falcatus R. Br.	+	Lu, Dios	–	(Cy), (Pg)	–	Wilson 5353, N.T.
S. fluitans Hook. f.†	–	Tr, Lu	–	–	Au	Beauglehole 6734, V.
S. hexandrus F. Muell. and Tate	–	Tr, Lu	–	–	Au	Whaite 4063, W. A.
S. latitans S. T. Blake	+	Tr, Lu	–	–	–	Wilson 2625, W.A.
S. moorei Benth.	+	Tr, Lu5ME	–	–	–	Coveny 11355, N.S.W.
S. paludosus (R. Br.) Poir.	+	–	–	–	–	Coveny 4871, N.S.W.
S. pleiostemoneus F. Muell.†	+	–	–	–	–	Wilson 2940, W.A.
S. scabripes Benth.†	+	–	–	–	–	Wilson 4511, N.S.W.
S. sesquispiculus C. B. Clarke	+	Tr	–	–	Au	Newbey 4207, W.A.
S. sparteus R. Br.	–	Tr	–	Cy, Pg, Dp	Au	Wilson 5169, N.T.
S. subaphyllus Kük.	+	Lu	–	–	Au	Cunningham and Milthorpe 4244, N.S.W.
S. subflavus s. lat.	–	Lu5ME	Qu	–	–	Wilson 2603, W.A.
S. subflavus s. lat.	+	Lu5ME	Qu, flavonol methyl ethers	–	–	Wilson 2776, W.A.
S. subflavus s. lat.	+	Lu	Qu	–	–	Wilson 2811, W.A.

S. submicrostachyus Kük.	–	Tr	–	–	Au	Wilson 2830, W.A.
S. unispiculatus F. Muell. ex. Benth.	+	Tr,DK/DK, unident.	–	Cy	Au	Wilson 2720, W.A.
Schoeneus sp. 'A'	–	Lu, 7,3,4'-triOH, DK/DK and B/Y unident.	–	–	–	Wilson 2785, W.A.
Mesomelaena graciliceps (C. B. Clarke) K. L. Wilson	+	Tr	–	–	Au	Wilson 2869, W.A.
M. preissii Nees	(+)	Lu5ME	Qu (Isorh, Km)	–	–	Wilson 2713, W.A.
M. pseudostygia (Kük.) K. L. Wilson	–	Tr	Qu, Isorh	–	–	Wilson 2632, W.A.
M. stygia (R. Br.) Nees subsp. *stygia*	(+)	Lu, Lu7ME	Qu, (Isorh or Km), flavonol methyl ether	–	–	Wilson 2993, W.A.
M. tetragona (R. Br.) Benth.	+	Tr, Lu, Ap	–	–	–	Wilson 2872, W.A.
Gymnoschoenus anceps (R. Br.) Nees	–	–	–	–	–	Wilson 3039, W.A.
G. sphaerocephalus (R. Br.) Hook. f.	–	Lu	–	(Cy)	–	Wilson 4385, N.S.W.
Carpha alpina R. Br.	–	Tr, Lu	–	(Cy)	–	Thompson 4018, N.S.W.
C. nivicola F. Muell.	–	Tr, Lu	–	Cy, Dp	–	Thompson 4506, N.S.W.
Tetraria capillaris (F. Muell.) J. M. Black	+	Tr, Aca	(Qu) Flavonol methyl ethers	–	–	McBarron 10309, N.S.W.
T. capillaris (F. Muell.) J. M. Black	(+)	Tr, Aca	Qu	–	–	Wilson 2989, W.A.
T. octandra (Nees) Kük.	+	–	–	(Cy)	–	Wilson 3062, W.A.
Lepidosperma carphoides F. Muell. ex. Benth.	–	–	–	–	–	Wilson 2795, W.A.
L. costale Nees	–	Tr, Lu5ME	Isorh, flavonol methyl ethers	–	–	Coveny 7967
L. effusum s. lat.	–	Tr	Qu, Isorh	–	–	Wilson 3017, W.A.
L. filiforme Labill.	–	Tr	Qu, Isorh	Cy, Pg, Dp	–	Wilson 4394, N.S.W.
L. flexuosum R. Br.	–	Tr, Lu	Qu, Isorh, flavonol methyl ethers	–	–	Constable 5561, N.S.W.
L. forsythii A. A. Hamilton	+	Tr, Lu	–	–	+ (not Au)	Coveny 11203, N.S.W.
L. laterale s. lat. }	–	Tr	–	–	–	Wilson 3696, Q.
L. laterale s. lat. }	+	–	(Qu)	Cy, Pg	–	Wilson 4419, N.S.W.
L. lineare s. lat.	–	Tr	Qu, Isorh	–	–	Beauglehole 24865, V.
L. neesii Kunth	+	Tr	–	–	–	Coveny 11126, N.S.W.
L. pruinosum Kük.	–	Tr	Qu, Isorh	–	–	Wilson, 2579, W.A.
L. urophorum N. A. Wakefield }	–	Tr	–	–	–	Coveny 11598, N.S.W.
L. urophorum N. A. Wakefield ('N.C. form') }	–	–	–	–	–	Wilson 4499, N.S.W.
Lepidosperma ustulatum Steudel	–	(Tr), (Dios)	Qu, Isorh, Qu3ME, Km3ME, Qu 3,7DIME, (Km 3,7DIME)	–	–	Wilson 2991, W.A.
Lepidosperma sp. H	–	Tr	Qu	(Cy)	–	Wilson 2834, W.A.
Lepidosperma sp. I	–	Tr	(Qu), (Isorh)	–	–	Wilson 3015, W.A.

Table 1. (*Continued*)

Sub-family, tribe,* genus and species	Flavone *C*-glycosides	Flavones	Flavonols	Proantho-cyanidins	Aurones	Collector's name, No. and State of collection
Lepidosperma tenue Benth.	–	Tr	Qu, Isorh	–	–	Wilson 2718, W.A.
Lepidosperma sp. U_1	–	Tr	Qu, Isorh	–	Chalcone + flavanone present	Wilson 2891, W.A.
Tricostularia compressa Nees	+	–	–	–	+ not Au	Wilson 2932, W.A.
T. neesii Lehm.	+	Tr, Aca	–	–	Au	Wilson 2810, W.A.
T. pauciflora (R. Br.) Benth.	+	–	–	–	Au	Coveny 11036 and James, N.S.W.
T. pauciflora (R. Br.) Benth.	+	(Tr)	–	–	Au	Coveny 11357, N.S.W.
T. undulata (Thwaites) Kern	+	Lu	–	Cy, Pg, Dp	Au	Wilson 5149, N.T.
Cladium procerum S. T. Blake	+	(Lu), B/Y, unident.	–	Pg	–	Wilson 3959, N.S.W.
Baumea juncea (R. Br.) Palla	+	–	–	Cy, Pg	Au	Wilson 3970, N.S.W.
B. nuda (Steudel) S. T. Blake	+	Tr	–	(Cy)	–	Coveny 11423, N.S.W.
B. rubiginosa (Spreng.) Boeck.	–	(Tr)	Qu, Km, My	Cy	–	Wilson 4388, N.S.W.
B. teretifolia (R. Br.) Palla	–	Tr, Lu5ME	–	Cy	–	Wilson 4398, N.S.W.
Caustis blakei Kük.	+	DK/DK, unident.	–	–	–	Wilson 4010, N.S.W.
C. dioica R. Br. ♂	+	Tr, Lu	DK/DK, unident.	–	–	Whaite 4307, W.A.
C. dioica R. Br. ♀	+	Tr, Lu, 2 B/Y, unident.		–	–	
C. flexuosa R. Br.	+	Tr, Ap	–	Cy	–	Coveny 11035, N.S.W.
C. flexuosa R. Br. form	+	Tr, Lu, DK/DK, unident.	Qu	Cy, Cp	Au	Wilson 4510, N.S.W.
C. recurvata Spreng.	+	Tr, Lu	–	Cy, Pg	–	Wilson 4009, N.S.W.
Evandra aristata R. Br.	–	Lu, Ap	–	–	Au	Phillips CBG 034026, W.A.
E. aristata R. Br.	–	Lu, Ap	–	–	–	Wilson 2956, W.A.
Gahnia aspera (R. Br.) Spreng	–	Tr, Lu	–	–	–	Wilson 3447, Q.
G. deusta (R. Br.) Benth.	–	Tr, Lu	–	–	–	Wilson 3145, S.A.
G. filifolia (Presl.) Kük. ex. Benth.	–	Tr, Lu	DK/DK, unident.	–	–	Coveny 11599, N.S.W.
G. lanigera (R. Br.) Benth.	–	Tr, B/Y unident.	2 Fl'Y, unident.	–	–	Wilson 3144, S.A.
G. microstachya Benth.	–	Tr, Lu, Chrys, B/Y, unident.	Fl'Y, unident.	Cy	–	Coveny 11372, N.S.W.
G. radula (R. Br.) Benth.†	–	Tr, Lu	–	(Cy)	Au	Wilson 3910, N.S.W.
G. sieberiana Kunth.	+	Tr, Lu	Qu, 3ME, Km 3ME, Qu 3,7,4'tri ME?	Cy	Au	Wilson 4420, N.S.W.
G. subaequiglumis S. T. Blake	–	Tr, Lu	Qu 7,3,4'tri ME?	–	Au	Wilson 4421, N.S.W.
Reedia spathacea F. Muell.	–	Lu, Lu5ME	Qu (Km)	–	–	Wilson 3010, W.A.
Arthrostylis aphylla R. Br.	–	Tr	–	–	–	Powell 753, Q.
Ptilanthelium deustum (R. Br.) Kük.	–	Tr	Flavonol methyl ether	–	Au	Wilson 4512, N.S.W.

Rhynchospora brownii R. and S.	+	Tr, Lu	Flavonol methyl ether	–	–	Wilson 4517, N.S.W.
R. heterochaeta S. T. Blake	+	Tr	–	–	–	Wilson 3672, Q.
R. leae C. B. Clarke	+	Tr	–	–	–	Wilson 3672a, Q.
R. rubra (Lour.) Makino	+	Tr	–	–	–	Wilson 3673, Q.
Trachystylis stradbrokensis (Domin) Kük.	–	Tr	–	(Cy)	–	Jacobs 3975, Q.
Oreobolus distichus F. Muell. }	+	Tr	–	Cy	(Au)	Thompson 4510, N.S.W.
O. distichus F. Muell. }	(+)	Tr	–	Cy	Au	Thompson 4515, N.S.W.
O. pumilio R. Br.	(+)	Tr	Qu	Cy	Au	Thompson 4501, N.S.W.
Cyathochaeta avenacea (R. Br.) Benth.	–	Tr	Qu, Isorh	–	–	Tindale 340, W.A.
C. diandra (R. Br,) Nees	–	Tr, Lu	–	Cy	–	Wilson 5619, N.S.W.
Cypereae						
Cyperus						
Sub-genus *Anosporum*						
Section *Graciles*						
Cyperus enervis R. Br.†	–	Tr, Ap?	–	Cy	–	Wilson 4082, N.S.W.
C. sculptus S. T. Blake	–	Tr	–	Cy	–	Wilson 4095, N.S.W.
C. trinervis R. Br.	–	Tr, Lu5ME	–	Cy	–	Wilson 3995, N.S.W.
Sub-genus *Cyperus*						
Section *Iriae*						
Cyperus iria L.	–	Tr	–	Cy, Pg	Au	Wilson 5949, N.S.W.
Sub-genus *Mariscus*						
Section *Thunbergiana*						
Cyperus congestus Vahl	–	Tr, Lu	–	Cy	–	Wilson 5695, N.S.W.
Section *Pinnati*						
C. sp. F.	–	Tr, Lu	–	Cy	Au	Wilson 5500, Q.
C. gunnii Hook. f.	–	Tr	–	–	Au	Wilson 4439, N.S.W.
C. microcephalus (form) }	–	Tr, Lu	–	Cy, Dp	Au	Wilson 5202, N.T.
C. microcephalus (form) }	–	Tr	–	–	Au	Wilson 5303, N.T.
C. oxycarpus S. T. Blake	–	–	–	Cy, Pg	Au + one unident.	Wilson 5240, N.T.
Subgenus *Kyllinga*						
Section *Kyllinga*						
C. sesquiflorus (Torr.) Mattf. }	+	–	Qu, Km, Isorh	Cy, Pg	–	Wilson 4369, N.S.W.
C. sesquiflorus (Torr.) Mattf. }	+	–	Qu, Km, Isorh	(Cy), (Pg)	–	Wilson 4097, N.S.W.
C. sphaeroideus L. Johnson and O. Evans	–	Tr	Qu, Km	Cy, Pg	–	Wilson 4055, N.S.W.
Lipocarpha microcephala (R. Br.) Kunth	–	Tr, Lu5ME	Qu?	–	–	Wilson 4218, Q.
Schoenoplecteae						
Isolepis habra (Edgar) K. L. Wilson†	–	Tr	–	–	–	Wilson 2305, N.S.W.
I. hookeriana Boeck.†	–	Tr	–	–	–	Beauglehole 34933, V.
I. humillima (Benth.) K. L. Wilson	–	Tr, Lu	–	–	–	Wilson 5280, N.T.
I. inundata R. Br.†	–	Tr	–	Cy	Au	Wilson 3932, N.S.W.
I. nodosa (Rottb.) R. Br.	–	Tr	–	–	(Au)	Wilson 4536, N.S.W.
I. platycarpa (S. T. Blake) Soják	–	Tr, Lu	–	(Cy)	Au	Wilson 4361, N.S.W.

Table 1. (*Continued*)

Sub-family, tribe,* genus and species	Flavone *C*-glycosides	Flavones	Flavonols	Proantho-cyanidins	Aurones	Collector's name, No. and State of collection
I. producta (C. B. Clarke) K. L. Wilson	–	Tr	–	–	–	Briggs 1379, N.S.W.
I. producta (C. B. Clarke) K. L. Wilson	–	Tr, Lu	–	–	–	Wilson 4471, N.S.W.
I. prolifera (Rottb.) R. Br.†	–	Tr	–	–	Au	Wilson 4532, N.S.W.
I. sepulcralis Steudel	–	Tr, Lu	–	–	–	Coveny 11422, N.S.W.
Hymenochaeta grossa (L.f.) Nees	+	Tr, B/Y, unident	–	Cy, Dp	–	Wilson 5100, N.T.
Bolboschoenus caldwellii (V. J. Cook) Soják	–	Tr, Lu, Ap, Lu5ME	Qu3ME	Cy	–	Wilson 4535, N.S.W.
B. fluviatilis (Torrey) Soják	+	Tr, Lu	–	–	–	Coveny 11476, N.S.W.
Schoenoplectus dissachanthus (S. T. Blake) J. Raynal	+	Tr	–	–	–	Latz 4916, N.T.
S. laevis (S. T. Blake) J. Raynal	(+)	Tr	Flavonol methyl ether	–	–	Dunlop 5405, W. A.
S. mucronatus (L.) Palla ex. Kerner }	–	Tr	–	–	–	Coveny 11463, N.S.W.
S. mucronatus (L.) Palla ex. Kerner }	+	Tr	Flavonol methyl ether	–	–	Wilson 4501, N.S.W.
S. validus (Vahl) A. Löve and D. Löve	–	Tr	Qu, Km	Cy, Pg	–	Wilson 4278, Q.
Fuirena ciliaris (L.) Roxb.	–	–	Qu, Km, Isorh	–	–	Wilson 3868, N.S.W.
F. incrassata S. T. Blake	–	–	Qu, Km, Isorh	–	–	Wilson 3563, Q.
Scirpeae						
Scirpus polystachyus F. Muell.	+	Tr, Lu	–	–	–	Coveny 11602, N.S.W.
Fimbristylideae						
Eleocharis brassii S. T. Blake	+	Tr	–	Cy, Pg	–	Wilson 5318, N.T.
Eleocharis sp. aff. *brassii*	+	Tr	–	–	Au + one unident.	Wilson 4845, W.A.
E. cylindrostachys Boeck. }	+	Tr	–	Cy (Pg) Dp	–	Wilson 4140, N.S.W.
E. cylindrostachys Boeck. }	–	Tr	–	–	Au	Wilson 4335, N.S.W.
E. dietrichiana Boeck.	+	Tr, Lu	Qu	(Cy)	–	Wilson 3875, N.S.W.
E. equisetina Presl†	–	Tr	–	(Cy) (Pg)	Au	Wilson 3825, Q.
E. geniculata (L.) R. and S.	–	Tr, Lu, Lu5ME	Flavonol methyl ether	(Cy)	–	Wilson 5527, Q.
E. minuta Boeck.	–	Tr, Lu, Lu5ME	–	–	–	Wilson 3976, N.S.W.
E. pallens S. T. Blake }	–	Tr	Qu, Km	Cy, Pg	–	Wilson 3522, Q.
E. pallens S. T. Blake }	–	Tr	Qu, Km	Cy, Pg	Au	Wilson 4329, N.S.W.
E. pusilla R. Br.†	+	Tr, Lu	–	–	–	Coveny 11443, N.S.W.
E. sphacelata R. Br. }	–	Tr, Lu	Qu	Cy, Dp	Au	Wilson 4528, N.S.W.
E. sphacelata R. Br. }	–	Tr	Flavonol methyl ether	–	(Au)	Coveny 11451, N.S.W.
Fimbristylis sp. aff. *arthrostyloides*	–	Tr	(Qu) Flavonol methyl ethers,	Cy	–	Wilson 5230, N.T.
F. bisumbellata (Forsk.) Bubani	+	–	Qu	–	–	Sharpe 1562, Q.

F. caespitosa R. Br.†	–	(Tr)	Fl′Y/O, unident.	–	(Au)	Latz 7083, N.T.
F. cephalophora F. Muell.	+	Tr	–	–	(Au)	Latz 5413, N.T.
F. corynocarya F. Muell.	–	2 DK/DK, unident.	–	–	–	Wilson 5537, Q.
F. dichotoma (L.) Vahl }	+	Tr	–	–	–	Wilson 4016, N.S,W.
F. dichotoma (L.) Vahl }	+	Tr	–	–	–	Wilson 4228, Q.
F. dichotoma (L.) Vahl }	+	Tr	–	Cy, Dp	–	Wilson 4519, N.S.W.
F. eremophila Latz	+	Tr	(Qu)	–	–	Latz 8714, N.T.
F. ferruginea (L.) Vahl†	–	Tr	–	–	–	Wilson 3968, N.S.W.
F. littoralis Gaudich.	+	Tr	–	–	–	Maconochie 2596, N.T.
F. macrantha F. Muell.	–	Tr, Lu	Flavonol methyl ether	–	Au	Wilson 4971, N.T.
F. nuda Boeck.	+	–	–	–	–	Latz 7179, N.T.
F. nutans (Retz.) Vahl	–	Tr	–	(Cy)	–	Wilson 4034, N.S.W.
F. oxystachya F. Muell.	–	Tr, Lu	Flavonol methyl ethers	–	–	Latz 8667, N.T.
F. pachyptera S. T. Blake	–	Tr, Lu	–	Cy	Au	Wilson 5207, N.T.
F. schultzii Boeck.	–	Tr	–	(Cy)	–	Wilson 4757 and Barker, N.T.
F. squarrulosa F. Muell.	–	Tr, Lu	Flavonol methyl ethers	Cy	Au	Wilson 4888, N.T.
F. tetragona R. Br.	–	B/LB, unident.	Qu, Km	–	–	Wilson 4713, N. T.
Bulbostylis barbata (Rottb.) C. B. Clarke	+	Tr	(Qu)	–	–	Wilson 3142, N.S.W.
B. densa (Wallich) Hand.-Mazz.	+	Tr	–	Cy, Pg	–	Wilson 4351, N.S.W.
Crosslandia setifolia W. V. Fitzg	+	Tr	Qu	–	–	Lazarides and Adams 8, N.T.
CARICOIDEAE						
Sclerieae						
Scleria brownii Kunth }	+	–	Qu, Km	Cy, Pg, Dp	(Au)	Wilson 3626, Q.
S. brownii Kunth }	+	–	Qu, Km	Cy	Au	Wilson 3433, Q.
S. caricina (R. Br.) Benth.	+	–	–	–	–	Blake 9652, Q.
S. mackaviensis Boeck.† }	+	–	Qu, Km	(Cy)	Au	Wilson 4415, N.S.W.
S. mackaviensis Boeck.† }	+	–	Qu, Km	Cy, Pg	–	Wilson 4195, Q.
S. novaehollandiae Boeck.	–	Tr, Lu	–	–	–	Wilson 3687, Q.
S. pygmaea R. Br. }	+	–	–	–	–	Wilson 5215, N.T.
S. pygmaea R. Br. }	+	–	–	–	–	Jacobs 1806, N.T.
Scleria sp. aff. *pygmaea* }	+	–	–	–	–	Wilson 5055, N.T.
S. rugosa R. Br.	–	Lu, Dios	–	–	–	Wilson 3688, Q.
S. sphacelata F. Muell.	+	Tr	–	Cy, Pg, Dp	Au	Wilson 3407a, Q.
S. tricuspidata S. T. Blake	+	(Tr), Lu, Ap	–	–	(Au)	Wilson 3687a, Q.
Cariceae						
Uncinia sp. aff. *compacta*	–	Tr, Lu, 7.3′,4′-triOH	–	–	–	Thompson 4502, N.S.W.
Uncinia sp. aff. *silvestris*	–	Tr, Lu	Flavonol methyl ethers	–	–	Coveny 5913, N.S.W.
Carex appressa R. Br. }	+	Tr, Lu	–	–	–	Wilson 4438, N.S.W.
C. appressa R. Br. }	+	Tr, Lu5ME, B/Y, unident.	–	–	–	Thompson 4504, N.S.W.

Table 1. (*Continued*)

Sub-family, tribe,* genus and species	Flavone *C*-glycosides	Flavones	Flavonols	Proantho-cyanidins	Aurones	Collector's name, No. and State of collection
C. declinata Boott	–	Tr	–	–	–	Wilson 4170, N.S.W.
C. fasicularis Soland. ex. Boott	+	Tr, Lu	–	–	–	Wilson 4468, N.S.W.
C. gaudichaudiana Kunth.	+	Tr	–	–	–	Wilson 4461, N.S.W.
C. hattoriana Nakai ex. Tuyama	(+)	Tr, Lu5ME	–	–	–	Wilson 4080, N.S.W.
C. hebes Nelmes	+	Tr, Lu, 7,3′,4′-triOH	–	–	–	Thompson 4503, N.S.W.
C. inversa R. Br.	–	Lu5ME	Qu, Km	–	–	Wilson 3411, Q.
C. inversa R. Br.	–	Tr, Lu5ME	Qu	–	–	Wilson 4187, Q.
C. jackiana Boott	+	(Tr)	–	–	–	Thompson 4509, N.S.W.
C. longebrachiata Boeck.†	+	7,3′,4′-triOH	–	–	–	Wilson 4460, N.S.W.

*Classification as devised and used in the National Herbarium of N.S.W.

†Flavonoid sulphates also present.

Key: Tr, tricin; Lu, luteolin; Lu5ME, luteolin 5-methyl ether; Ap, apigenin; Aca, acacetin; Chrys, chrysoeriol; Dios, diosmetin; Lu7ME, luteolin 7-methyl ether; 7,3′,4′-triOH, 7,3′,4′-trihydroxyflavone; Qu, quercetin; Qu3ME, quercetin 3-methyl ether; Qu 3,7DIME, quercetin 3,7-dimethyl ether; Qu 3,7,4′-triME, quercetin 3,7,4′-trimethyl ether; Isorh, isorhamnetin; My, myricetin, Km, kaempferol; Km 3ME, kaempferol 3-methyl ether; Km 3,7diME, kaempferol 3,7-dimethyl ether; flavonol methyl ethers, unidentified compounds which have similar R_f and colour properties in UV light to flavonol methyl ethers; Cy, cyanidin; Pg, pelargonidin; Dp, delphinidin; Au, aureusidin; Q., Queensland; N.S.W., New South Wales; V., Victoria; N.T., Northern Territory; W.A., Western Australia; S.A., South Australia ( ), trace constituent; DK/DK, dark to dark in UV light plus ammonia; B/Y, blue to yellow in UV plus ammonia; Fl′Y, fluorescent yellow in UV; Fl′Y/O, fluorescent yellow to orange in UV plus ammonia; B/LB, blue to light blue in UV plus ammonia; unident., unidentified constituent.

Table 2. The distribution of flavonoid aglycones in the inflorescences (including fruits) of Australian Cyperaceae

Sub-family, tribe, genus and species	Glycosylflavones	Flavones	Flavonols	Aurones	Carexidin
CYPEROIDEAE					
Hypolytreae					
Hypolytrum nemorum	–	–	–	–	–
*Exocarya sclerioides**	–	–	–	Aurones 1 and 2	–
Lepironia articulata	–	Lu	–	Au	+
Chorizandra cymbaria	–	–	–	Aurone 1	–
C. sphaerocephala	–	–	–	Aurone 1	–
Chrysitrix distigmatosa	–	–	–	–	–
Rhynchosporeae					
Schoenus apogon (4309)	–	unident.	–	Au	–
S. apogon (4328)	–	Lu	–	Au	–
S. apogon (4395)	–	–	–	–	–
S. asperocarpus	–	Tr, Lu	–	Au	–
S. bifidus	–	Tr, Lu	–	–	–
S. brevifolius	–	Lu	–	–	+
S. sp. aff. *brevisetis*	–	–	–	Au	–
S. calostachyus	–	Lu	–	Au	–
S. curvifolius	–	Lu	–	Au	–
S. ericetorum	–	–	–	Au	–
S. falcatus	–	unident.	–	Au	–
S. fluitans	–	Lu, Ap	–	–	–
S. hexandrus	–	Lu	–	Au	–
S. moorei	–	–	–	–	–
S. paludosus	+	Lu	–	Au	+
S. pleiostemoneus	–	–	–	–	–
S. scabripes	–	Lu	–	Au	+
S. sesquispiculus	–	Lu	–	Au	–
S. sparteus	–	–	–	Aurone 1	–
S. subaphyllus	–	Lu	–	Au	–
S. subflavus (2603)	–	–	–	–	–
S. subflavus (2776)	–	unident.	–	–	–
S. subflavus (2811)	–	Lu	–	–	–
S. submicrostachyus	–	–	–	Au	–
S. unispiculatus	–	Tr (as 5G)	Methyl ethers	Au	–
Mesomelaena graciliceps	–	–	–	Au	–
M. preissii	–	–	–	–	–
M. pseudostygia	–	–	–	Au	–
M. stygia	–	–	–	–	–
M. tetragona	–	Lu	–	–	–
Gymnoschoenus anceps	–	Lu	–	–	–
G. sphaerocephalus	–	Lu (as 5G)	–	–	–
Carpha alpina	–	Tr, Lu	–	–	–
C. nivicola	–	Tr, Lu	–	Au	–
Tetraria capillaris	–	–	–	–	–
T. octandra	–	Tr, Lu	Qu	–	–
Lepidosperma carphoides	–	–	–	–	–
L. costale	–	–	Qu, Km, Isorh	–	–
L. effusum	–	–	–	–	–
L. filiforme	–	–	Qu	–	–
L. flexuosum	–	–	–	–	–
L. forsythii	–	–	–	–	–
L. laterale (3696)	–	–	Km	–	–
L. laterale (4419)	–	–	–	Au	–
L. lineare	–	–	–	–	–
L. neesii	–	–	–	–	–
L. pruinosum	–	Lu	–	–	–
L. urophorum (4499)	–	unident.	–	–	–
L. urophorum (11598)	–	–	–	–	+
L. ustulatum	–	–	–	–	–
L. sp. H	–	–	Qu	–	–
L. sp. I	–	–	–	Au	+

Table 2. (*Continued*)

Sub-family, tribe, genus and species	Glycosylflavones	Flavones	Flavonols	Aurones	Carexidin
L. tenue	–	Lu	Qu	–	–
L. sp. U_1	–	–	–	–	–
Tricostularia compressa	–	Lu	–	Au	–
T. neesii	–	Tr	–	–	–
T. pauciflora (11036)	+	–	–	Au	–
T. undulata	+	–	–	Au	–
Cladium procerum	–	–	–	Au	–
Baumea juncea	–	–	–	Au	–
B. nuda	–	–	–	–	–
B. rubiginosa	–	Lu	Qu, My	–	–
B. teretifolia	–	–	–	–	–
Caustis blakei	–	Lu	–	Au	–
C. dioica	+	Tr, Lu	–	Au	+ (stem)
C. flexuosa (11035)	+	–	–	–	–
C. flexuosa (265)	–	Tr, Lu	Qu	Au	–
C. recurvata	–	Lu	–	–	–
Evandra aristata (034026)	–	–	–	–	–
E. aristata (2956)	–	–	–	–	–
Gahnia aspera	–	–	–	–	–
G. deusta	–	Lu	–	Au	–
G. filifolia	–	–	–	Au	–
G. lanigera	–	–	–	Au	–
G. radula†	–	Lu	–	–	–
G. subaequiglumis	–	–	–	Au	–
G. sieberiana	–	Lu	–	Au	–
Reedia spathacea	–	–	–	–	–
Arthrostylis aphylla	–	–	–	–	–
Ptilanthelium deustum	–	–	–	Au	–
Rhynchospora brownii	–	Tr, Lu	–	–	–
R. heterochaeta	–	Lu	–	–	–
R. leae	–	–	Methyl ethers	–	–
R. rubra	–	Lu	–	–	–
Trachystylis stradbrokensis	–	–	–	–	–
Oreobolus distichus	–	–	–	–	–
O. pumilio	–	–	–	–	–
Cyathochaeta avenacea	–	–	–	–	–
C. diandra	+	Lu	–	Au	–
C. oxycarpus	–	–	–	Au	–
Cypereae					
Cyperus enervis	–	Lu	–	–	–
C. sculptus	–	–	–	–	–
C. trinervis	–	–	Km	–	–
C. iria	–	Lu	Qu	Au, Mt	–
C. congestus†	–	Lu	–	Au	–
C. sp. F.	–	Lu	–	Au, Mt	–
C. gunnii	–	Tr, Lu	–	–	–
C. microcephalus (5202)	–	Tr, Lu	–	Au, Mt	–
C. microcephalus (5303)	–	Tr, Lu	–	Au, Mt	+
C. oxycarpus	–	–	–	Au	–
C. sesquiflorus (4369)	–	–	Km, Qu	–	–
C. sesquiflorus (4097)	–	–	–	–	–
C. sphaeroideus	–	Lu	Qu	–	–
Lipocarpha microcephala	–	Lu, Ap	–	Au	–
Schoenoplectreae					
Isolepis habra†	–	unident.	–	–	–
I. hookeriana†	–	Lu	–	–	–
I. humillima†	–	Tr, Lu	–	Au	+
I. inundata†	–	unident.	–	–	–
I. nodosa	–	–	–	Au	–
I. platycarpa	–	–	–	–	–
I. producta (1379)	–	Lu (as 5G)	–	–	–

Sub-family, tribe, genus and species	Glycosylflavones	Flavones	Flavonols	Aurones	Carexidin
I. producta (4471)	–	–	–	–	–
I. prolifera†	–	Tr	–	Au	–
I. sepulcralis	–	–	–	–	–
Hymenochaeta grossa	–	Tr, Lu	–	Au	–
Bolboschoenus caldwellii	–	Lu	–	–	–
B. fluviatilis	–	Lu	–	–	–
Schoenoplectus dissachanthus	–	–	–	Au	–
S. mucronatus (11463)	–	–	–	Au	–
S. mucronatus (4501)	–	–	–	–	–
S. laevis	–	Lu	–	–	–
S. validus	–	–	Qu	–	–
Fuirena ciliaris	–	–	Qu	–	–
F. incrassata	–	–	Qu	–	–
Scirpeae					
Scirpus polystachyus	–	–	–	–	–
Fimbristylideae					
Eleocharis brassii	–	Tr, Lu	–	Au	–
E. sp. aff. *brassii*	–	–	–	Au, aurone 1	–
E. cylindrostachys (4140)	–	–	Qu	Au	–
E. cylindrostachys (4335)	–	–	Qu	Au	–
E. dietrichiana	–	–	–	–	–
E. equisetina	–	–	–	Au	–
E. geniculata	–	Tr, Lu	–	–	–
E. minuta	–	–	–	–	–
E. pallens (3522)	–	–	–	Au	–
E. pallens (4329)	–	–	Km, Qu	Au	–
E. sphacelata (4528)	–	–	–	Au	–
E. sphacelata (11451)	–	Tr (as 5G)	–	Au	–
Fimbrystylis sp. aff. *arthrostyloides*	–	Tr	–	Au	–
F. bisumbellata	–	–	–	–	–
F. caespitosa	–	–	unident.	Au	–
F. cephalophora	–	–	–	Au	–
F. corynocarya	–	–	–	–	–
F. dichotoma (4016)	–	Tr, Lu	Methyl ethers	Au	–
F. dichotoma (4228)	–	Tr	Methyl ethers	Au	–
F. dichotoma (4519)	–	Tr, Lu	Methyl ethers	Au	–
F. eremophila	–	–	–	Au	–
F. ferruginea†	+	–	–	Au	–
F. littoralis	–	Tr	–	–	–
F. macrantha	–	Tr (as 5G)	–	Au	–
F. nuda	–	–	–	–	–
F. nutans	–	unident.	–	Au	–
F. oxystachya	–	Tr	–	–	–
F. pachyptera	–	Tr	Methyl ethers	–	–
F. schultzii	+	Tr	–	–	–
F. squarrulosa	–	Tr	–	–	–
F. tetragona	–	Tr, Lu	Qu, Km	–	–
Bulbostylis barbata	–	–	Qu	Au	–
B. densa	–	–	–	Au	–
Crosslandia setifolia	–	Tr	–	–	–
CARICOIDEAE					
Sclerieae					
Scleria brownii (3626)	–	–	Qu, Km	Au	–
S. brownii (3433)	–	–	–	Au	–
S. mackaviensis (4415)	–	–	–	Au	–
S. mackaviensis (4195)	–	–	Qu, Km	–	–
S. novaehollandiae	–	Lu	–	Au	–
S. pygmaea (5215)	+	–	–	Au	–
S. pygmaea (1806)	+	–	–	Au	+
S. aff. *pygmaea*	+	–	–	–	–
S. rugosa	–	–	–	–	–

Table 2. (*Continued*)

Sub-family, tribe, genus and species	Glycosylflavones	Flavones	Flavonols	Aurones	Carexidin
S. sphacelata	–	unident.	–	Au	+
S. tricuspidata	–	Lu	Qu, Km	Au	–
Cariceae					
Uncinia sp. aff. *compacta*	–	Tr, Lu	–	–	–
Uncinia sp. aff. *sylvestris*	–	–	–	–	–
Carex appressa (4438)	–	–	–	Sulphuretin	–
C. appressa (4504)	–	Tr	–	–	–
C. declinata	–	–	–	–	–
C. fascicularis	+	Tr, Lu	–	–	–
C. gaudichaudiana	–	Tr, Lu	–	–	–
C. hattoriana	–	Lu	–	–	–
C. hebes	–	Tr, Lu	–	–	–
C. inversa (4187)	–	Lu	–	–	–
C. inversa (3411)	+	–	–	–	–
C. longebrachiata†	–	Tr, Lu	Qu	–	–

Key: as Table 1, except that *denotes the presence of flavonoid sulphates; Mt, mariscetin; 5G = 5-glycoside.

Table 3. Comparison of leaf flavonoid occurrences in Australian species: in the genus *Cyperus* and in other genera

Flavonoid	No. of species positive (and % frequency) in *Cyperus**	outside *Cyperus*†
Individual components		
Luteolin	73 (79%)	62 (39%)
Tricin	66 (72%)	120 (76%)
Luteolin 5-methyl ether	13 (14%)	14 (9%)
Apigenin	8 (9%)	5 (3%)
7,3′,4′-Trihydroxyflavone	—	4 (3%)
Diosmetin	—	2 (1%)
Acacetin	—	3 (2%)
Chrysoeriol	—	1 (1%)
Luteolin 7-methyl ether	—	2 (1%)
Class of compounds		
C-Glycosylflavones	4 (5%)	76 (48%)
Flavonoid sulphates	10 (11%)	17 (11%)
Flavonols (quercetin, kaempferol, isorhamnetin, myricetin)	10 (11%)	40 (25%)
Methylated flavonols	14 (15%)	23 (14%)
Procyanidins	46 (50%)	51 (32%)
Propelargonidins	—	17 (11%)
Prodelphinidins	—	12 (8%)
Aurones	34 (37%)	47 (29%)

*Species (92) surveyed, from ref. [4].
†Species (160) surveyed, from Table 1.

species closely related to *Scirpus* [7]. Additionally, vitexin has been found in the widespread tropical and sub-tropical species *Kyllinga brevifolia* by Huang *et al.* [8]. Similar compounds are probably widely present in the family, but further work is needed on their detailed characterization.

Luteolin and tricin seem to be as common in temperate as in tropical species among the Australian Cyperaceae (Tables 1 and 2), so that there is no obvious geographical variation in these flavonoid characters, unlike the results found previously for African species [3] and Australian *Cyperus* spp. [4]. What is apparent from this new survey is the occasional presence in quantity of various flavone methyl ethers. The presence of luteolin 5-methyl ether in the family was found to be characteristic of tropical rather than of temperate species in previous studies but luteolin 5-methyl ether occurred rarely in tropical species (other than *Cyperus* spp.) in this study and much more frequently in species with sub-tropical to temperate distributions. While the 5-methyl ether was found to occur in 14% of

Australian *Cyperus* spp. [4], its occurrence in other Australian genera is only 7% (Table 3). Several other methyl ethers, however, have been found for the first time in the Cyperaceae. Notable among these are luteolin 7-methyl ether, luteolin 4′-methyl ether (diosmetin) and acacetin, the 4′-methyl ether of apigenin. Additionally, chrysoeriol, which has been reported once before in *Trichophorum*, a northern temperate taxon [7], has now been found in the Australian *Gahnia microstachya* (Table 1). Finally, it may be noted that, although tricin and luteolin occur with equal frequency in *Cyperus*, in the family as a whole the descending order of frequency is: tricin (74%), luteolin and its methyl ethers (48%), and apigenin and its methyl ethers (5%).

Flavonols

Flavonols are significantly more frequent in the leaves of Cyperaceae generally than they are within the genus *Cyperus* (Table 3). Some 25% of the present sample (about equally tropical and temperate in distribution) have flavonols in the leaves. In general, flavonols are less common (in *ca* 10% of species) in the inflorescences (Table 2). Four common flavonols were encountered in acid hydrolysed extracts: quercetin, isorhamnetin, kaempferol and myricetin. Of these, quercetin is the most common, followed by isorhamnetin, its 3′-methyl ether. Kaempferol, by contrast, is quite rare and, when present, usually accompanies quercetin (e.g. in leaves and inflorescences of *Scleria* spp.). Myricetin has been found in only one genus *Baumea*. Here, it occurs in the leaves of *B. juncea* and in the inflorescence of *B. rubiginosa*. This is the only report so far of myricetin in the Cyperaceae.

The above flavonols mainly occur in sedges in *O*-glycosidic combination and 2D chromatograms of the plant extracts indicated that simple 3-glycosides are probably the major glycosidic type. These *O*-glycosides have not been studied in most cases, except that the 3-rutinoside of quercetin (rutin) was positively identified in the inflorescences of *Fuirena ciliaris* and *F. incrassata*.

Two of these flavonols, kaempferol and quercetin, were also detected in *Cyperus* leaves in the free state but in methylated form, e.g. as the 3,7-dimethyl ethers [4]. Similar partial methyl ethers were found during the present survey in some 14% of the species. Thus, these methyl ethers may be found elsewhere in the family rather than just within the genus *Cyperus*. Because of their lipid solubilities, they may occur free on the leaf surface, but this has yet to be established experimentally.

The distribution of flavonols in the Australian Cyperaceae is rather erratic at the generic level in both leaf and inflorescence. Flavonols most frequently occur in association with flavones but, where they do not, then some pattern may be discernible. For example, in *Scleria*, two species *S. brownii* and *S. mackaviensis*, have flavonols and lack flavones in the leaves, whereas the other five species studied have flavones but lack flavonols (Table 1). This pattern is similar in the inflorescences, except that *S. tricuspidata* is anomalous in having both flavones and flavonols (Table 2). At least one genus, *Fuirena*, seems to be distinctive in having only flavonols as the major constituents. In the present survey, *F. ciliaris* and *F. incrassata* were found to have quercetin in the inflorescences, and quercetin, kaempferol and isorhamnetin in the leaves. This ties in with our earlier findings of quercetin and kaempferol in *F. pubescens* [2], *F. pachyrrhiza* and *F. stricta* [3]. Other Cyperaceous genera with flavonols predominating include *Gahnia*, *Lepidosperma* and *Mesomelaena*. On the other hand, flavonols seem to be completely absent from *Carpha* (two species surveyed), *Evandra* (two samples of one species), *Gymnoschoenus* (two species), *Isolepis* (nine species) and *Tricostularia* (four species), and rare in *Carex* (in two of nine species).

Aurones

Yellow aurone pigments are the most characteristic class of flavonoid in the Cyperaceae, since they separate the family from other monocot groups, especially the Gramineae and the Juncaceae. Aurones were previously recorded in fruits or inflorescences of seven genera [1–3] and, in the recent survey of Australian *Cyperus*, they were found in inflorescences of over 55% of species and in the leaves of 37% [4]. In the present survey of other Australian genera, they were discovered in the inflorescences (and/or fruits) of 63 species (40% of sample) and in the leaves of 47 species (29% of sample). There are, thus, new records for 17 genera, bringing the total number of aurone-containing genera to 23 (Table 4). There is some correlation between presence in leaf and in inflorescence, but it is incomplete. In fact, in the leaves, aurones are equally common in tropical and temperate species, whereas in the inflorescences, they are more common in tropical than in temperate taxa.

The most common aurone of the Cyperaceae is aureusidin, 4,6,3′,4′-tetrahydroxyaurone [1–4] and the same pigment was found to occur widely during the present survey (Tables 1 and 2). Two other aurones, mariscetin and leptosidin, have also been reported in *Cyperus* [4], but neither of these compounds was encountered outside that genus. One further aurone, new to the family, namely sulphuretin (6,3′,4′-trihydroxyaurone) was found in only one sample, the inflorescence of *Carex appressa*. This was the only aurone recorded in tribe Cariceae. Other so far uncharacterized aurones were found during this survey, notably in inflorescences of *Exocarya* and *Chorizandra* and work is in progress on their identification. One pigment in *Fimbristylis cephalophora* has been tentatively identified as an aureusidin methyl ether but this identification needs confirmation.

Other flavonoids

Although stems, inflorescences and fruits in the Cyperaceae are often coloured, no ordinary anthocyanins

Table 4. Aurone distribution at generic level in inflorescences or fruits of the Cyperaceae

Previous records	Present work	Present work
Cyperus	*Baumea**	*Hymenochaeta*
*Eleocharis**	*Carex*	*Isolepis**
*Gahnia**	*Carpha*	*Lepidosperma*
Lepironia	*Caustis**	*Mesomelaena*
*Ptilanthelium**	*Chorizandra*	*Oreobolus*
Isolepis (as *Scirpus*)	*Cladium*	*Schoenoplectus*
*Schoenus**	*Evandra*	*Scleria**
	*Exocarya**	*Tricostularia**
	*Fimbristylis**	

*Also in the leaf.

have ever been encountered in the family and no evidence was obtained during the present survey of such pigments. There is, however, one related pigment, the so far incompletely characterized 3-desoxyanthocyanidin, carexidin. This substance is very readily detected in direct extracts by 2D chromatography, when it appears as an orange spot, which is bright yellow in UV light changing to bright red with ammonia. Its presence can be confirmed by electrophoresis at pH 2.2, when it moves towards the anode. Carexidin was originally found in *Carex riparia* inflorescences and then detected also in *C. acutiformis*, *Lepironia articulata*, *Scleria hebecarpa* and *Schoenus brevifolius* [1]. During the present survey (Table 2), it was again detected in new accessions of *L. articulata* and *Schoenus brevifolius*. In addition, it was detected *de novo* in the inflorescences of *Schoenus paludosus*, *S. scabripes*, two *Lepidosperma* spp., two *Scleria* spp., *Isolepis humillima* and in the stem of *Caustis dioica*. Thus, it is still quite rare, occurring in *ca* 5 % of species. At present, it is restricted to *Carex* and *Scleria* in the Caricoideae, *Caustis*, *Lepidosperma* and *Schoenus* of the Rhynchosporeae, *Isolepis* in the Schoenoplecteae and *Lepironia* in the Hypolytreae. Most of these are tropical plants, except for *Carex*.

By contrast with carexidin, proanthocyanidins based on pelargonidin, cyanidin and delphinidin are relatively widespread in the leaves of the Australian Cyperaceae, occurring in over one-third of the present sample (Table 1). Unlike *Cyperus* where only procyanidins were detected, other genera also contain propelargonidins and prodelphinidins. These condensed tannins have a fairly scattered occurrence throughout the family, but are present in the majority of genera (Table 1).

DISCUSSION

Flavonoid patterns of the Cyperaceae

The present survey, together with the results of earlier investigations, has shown that aurones are the most characteristic flavonoid features in the family. Additionally, it is clear that a considerable number of flavonoid structures are synthesized in the Cyperaceae. The number of aglycones detected in the family is now 25 (Table 5). The present survey, in particular, has indicated that *O*-methylation may occur at almost any of the hydroxyl groups of the common flavonoids. For example, the present discovery of the 7- and 4′-methyl ethers of luteolin means that all four possible monomethyl ethers of luteolin have been found. Flavonols, such as quercetin, may also carry methyl groups at every position, except perhaps the 5-hydroxyl. Extra hydroxylation is still rarely observed. The only two compounds of this type are 6-hydroxyluteolin from the South American genus *Lagenocarpus* [3] and sudachitin (5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone) from the northern temperate *Eriophorum* [7]; neither of these compounds was detected in the Australian samples. 5-Desoxyflavonoids are also uncommon, the only representatives being 7,3′,4′-trihydroxyflavone, mainly in *Cyperus* [4] inflorescences, and sulphuretin (6,3′,4′-trihydroxyaurone), newly reported from *Carex*.

Glycosidic patterns have not been examined yet in much detail, but several common glycosides are known to occur. These include the 7-glucosides of luteolin and tricin, and the 3-glucoside and 3-rutinoside of quercetin.

Table 5. Flavonoid aglycones present in the Cyperaceae

Flavones	Flavonols
Apigenin*	Kaempferol
4′-methyl ether (acacetin)	3-methyl ether
Luteolin*†	3,7-dimethyl ether
5-methyl ether	Quercetin†
7-methyl ether	3-methyl ether
3′-methyl ether (chrysoeriol)*	3′-methyl ether
4′-methyl ether (diosmetin)	(isorhamnetin)
7,3′,4′-Trihydroxyflavone	3,7-dimethyl ether
Tricin†	3,6,3′-trimethyl ether
6-Hydroxyluteolin	Myricetin
Sudachitin	3-Desoxyanthocyanidin
Aurones	Carexidin
Sulphuretin	
Aureusidin†	
Leptosidin	
Mariscetin	

*Present additionally in *C*-glycosidic combination.
†Widely occurring major constituent.

5-Glycosides of luteolin and tricin are also present occasionally. *C*-Glycosylflavones are also common, but have only been studied in detail in a few plants (see Results). Sulphated flavonoids were detected infrequently in this survey (in leaves of 17 species, in inflorescences of 10 species) and in earlier investigations. The frequency of sulphation still appears to be significantly less than in the related Juncaceae and Gramineae.

Taxonomic correlations

The Cyperaceae are commonly divided into the two sub-families, Cyperoideae (including Mapanioideae) and Caricoideae. Analysis of the flavonoid data indicates no marked differences between the two groups. It is true that flavone *C*-glycosides are much more common in leaves of the Caricoideae, while flavonol methyl ethers are mainly restricted to the Cyperoideae but there are only minor differences in other flavonoid characters. Variations at the tribal and generic levels are of more systematic interest and these will be considered as they occur in the seven tribes studied in order.

Only a small sample (six species in five genera) of the mainly tropical tribe Hypolytreae was examined (Tables 1 and 2). One may note that procyanidin is the only condensed tannin present, that tricin is rare and that few flavonoids, apart from aurones, occur in the inflorescences. However, the overall pattern is not markedly different from any other of the tribes and there is no chemical support for separating these taxa into their own sub-family, as has sometimes been suggested.

In the Rhynchosporeae, 10 genera have been surveyed and, in some cases, sampling at the generic level is high (24 species of *Schoenus*, 16 species of *Lepidosperma*). The most notable general feature of these plants is that *O*-methylated flavones and flavonols seem to be relatively common in the leaves. Most Australian Cyperaceae that have obvious viscid exudates belong to this tribe which may reflect the fact that the lipophilic methyl ethers are restricted to these exudates. Systematically, the flavonoid data are mainly of significance at the generic level. While

Schoenus shows no particular coherence in pattern, *Mesomelaena* is more distinctive. Classification of this genus has recently been revised by one of us [9]. It is interesting that *M. graciliceps*, morphologically the most distinctive species, is chemically different in the presence of aureusidin and the absence of flavonols. Furthermore, *M. stygia*, *M. preissii* and *M. pseudostygia*, previously treated as a single taxon *M. stygia*, are chemically different from each other.

Tricostularia (three species, represented by four samples, surveyed) is fairly distinctive with all samples having flavone *C*-glycosides and aurones but lacking flavonols. *Tricostularia undulata* (the only tropical species in the genus) is rather different in its leaf flavonoids, as well as in its morphology, from the other species, which are all confined to SW Australia. The two species of *Tetraria* examined (Table 1) differ in their chemistry, *T. capillaris* being distinguished by having acacetin in the leaves. *Tetraria octandra*, lacking both flavones and flavonols, is quite different chemically and, in fact, it may be better placed in a separate genus, *Tetrariopsis*, as suggested by Clarke [10]. Finally, in this tribe it may be seen that *Lepidosperma* has a fairly consistent flavonoid profile based on the presence of tricin, quercetin and isorhamnetin and almost complete absence of luteolin and of aurones.

In the Schoenoplecteae (five genera surveyed), the flavonoid data unequivocally indicate three groupings: *Isolepis*, sulphates characteristic, flavonols absent, glycosylflavones rare or absent; *Schoenoplectus*, *Bolboschoenus* and *Hymenochaeta*, flavonol methyl ethers characteristic, glycosylflavones present; and *Fuirena*, only flavonols present. The morphological relationships between *Schoenoplectus*, *Bolboschoenus* and *Hymenochaeta* are quite close and the chemical data are, thus, supportive of moves to unite these genera [9]. In the case of *Isolepis*, the flavonoid results indicate chemical uniformity within the genus as at present constituted and do not support the view that three species, *I. producta*, *I. nodosa* and *I. prolifera*, should be moved to other genera [11].

By contrast with the Schoenoplecteae, the Fimbristylideae (five genera surveyed) are much more uniform in flavonoid pattern and there are no consistent differences between genera. However, four species of *Fimbrystylis* (*F. macrantha*, *F. oxystachya*, *F. pachyptera* and *F. squarrulosa*) differ from other *Fimbrystylis* spp. surveyed in producing luteolin as well as tricin in their leaf tissue. These species are usually separated as the section *Abildgaardia*, but it has been suggested that the section should be given generic rank [12] and the present flavonoid data support this.

Flavonoid characters of the Sclerieae (eight *Scleria* species surveyed) would indicate that this tribe is chemically the most distinctive in the family. Thus, there are higher than average frequencies of *C*-glycosylflavones, flavonols, proanthocyanidins and aurones, and lower than average frequencies of flavones. The aurone aureusidin, in particular, was found in leaves of half the species and in the inflorescences of all but one. Within *Scleria* it may be noted that *S. caricina*, *S. pygmaea* and *S.* aff. *pygmaea* stand out from the rest in having glycosylflavones in both leaf and inflorescence and in otherwise lacking leaf constituents. These taxa have been moved into the genus *Diplacrum* and the chemical data would seem here to provide unambiguous support for such a separation. In fact, three other *Diplacrum* spp. surveyed earlier also had only glycosylflavones [3]. Eiten [13] has considered removing *Diplacrum* with *Calyptrocarya*, *Bisboeckeleria* and *Becquerelia* from the Sclerieae and placing them in a new tribe, the Bisboeckelerieae. The earlier chemical results are not in disagreement with this new alliance, except that two of the latter genera also contain luteolin 5-methyl ether.

Finally, the tribe Cariceae (11 species of two genera surveyed) has few flavonoid classes. The substances present are either flavones or glycosylflavones. No proanthocyanidins or aurones were detected and flavonols were only recorded in one species, *Carex inversa*. The simplification in flavonoid pattern and the presence of 5-desoxyflavonoids (sulphuretin in *Carex appressa* and 7,3′,4′-trihydroxyflavone in several species) in the Cariceae could be taken as signs of phylogenetic advancement. This would agree well with the morphological data since *Carex* is probably the most advanced genus in the family.

In conclusion, there are no dramatic correlations between flavonoid occurrences and the higher level classification of the Cyperaceae. However, it is apparent that more detailed studies within species groups of particular systematic complexity might yield several chemical characters that could be used in revisionary work. Geographically, several interesting correlations with flavonoid type [1–4] have been observed; the present work completes a representative survey of Australian taxa but wider sampling of the species of other continents is still needed. Chemically, the Cyperaceae are of continuing interest and a wealth of flavonoid structures remain to be elucidated in these plants.

EXPERIMENTAL

Plant material. Leaves and inflorescences were analysed separately from freshly dried plant material recently collected from natural populations growing in Australia. In those cases where leaf tissue was limited, stem tissue was also included in the leaf analysis. Voucher specimens are deposited in the National Herbarium of N.S.W. under the numbers shown in Table 1. The collector's name, number and State of origin are also given—further details are available from one of us (K.L.W.).

Flavonoid analysis. General procedures for the isolation and identification of flavonoid aglycones and glycosides in leaves and inflorescences are similar to those described in the previous paper on *Cyperus* spp. [4].

Identification of unusual flavonoid aglycones. Diosmetin and acacetin occurred in the free state and were isolated from 80% MeOH leaf extracts after purification in BAW on 3MM paper. They were identified by co-chromatography on TLC cellulose in BAW, Forestal, 50% HOAc and CAW (2:1) with authentic markers. Chrysoeriol was tentatively identified from the small quantity of compound available from R_f values and colour reactions in UV + NH_3 and with NA reagent compared with other flavone aglycones. An authentic sample of chrysoeriol was not available.

Luteolin 7-methyl ether, also found in the free state, was isolated and co-chromatographed as above but also on polyamide in toluene–MeCOEt–MeOH (4:3:3) with an authentic marker. Its colour in UV + NH_3 and with NA reagent (orange yellow) was also compared.

Aurones. Aureusidin, sulphuretin and mariscetin were detected by similar procedures as described before [4]. Several faster moving free aurones were detected, mainly in the inflorescences of several species and they are indicated in Table 2 as aurone 1, 2, etc. One such compound in *Fimbrystylis cephalophora* had identical spectral (UV λ_{max} 399 nm) and colour reactions to aureusidin but had consistently higher R_f ($\times$ 100) values (69 in BAW, 37 in CAW, 31 in 50% HOAc, 54 in Forestal) and could, thus, be an aureusidin methyl ether. This and other apparently novel aurones present are being further investigated.

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