Phytochemistry, Vol. 21, No. 10, pp. 2491–2507, 1982.
Printed in Great Britain.

0031-9422/82/102491-17$03.00/0
Pergamon Press Ltd.

FLAVONOIDS IN LEAVES AND INFLORESCENCES OF AUSTRALIAN *CYPERUS* SPECIES

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(*Received* 22 *February* 1982)

Key Word Index—*Cyperus*; Cyperaceae; flavonoids; aurones; aureusidin; tricin; luteolin 5-methyl ether; 7, 3′, 4′-trihydroxy flavone; flavonol methyl ethers; mangiferin; chemotaxonomy.

Abstract—A survey of the flavonoids of some 92 species of Australian *Cyperus*, mainly of subtropical or tropical origin, has confirmed a correlation previously reported in this family between flavonoid pattern and plant geography. The pattern found was similar to that of African and South American Cyperaceae, particularly in the occurrence of the rare marker substance, luteolin 5-methyl ether. Tricin and luteolin are relatively common, in glycosidic form, in the leaves while the flavonol quercetin is infrequent. When present, quercetin occurs either in glycosidic form or free as a methyl ether. The 3-monomethyl and 3, 7-dimethyl ethers of kaempferol and quercetin and the 3, 7, 3′-trimethyl ether of quercetin are reported for the first time from the Cyperaceae. The flavonoid pattern of inflorescences is distinct from that of the leaves in that tricin is not detectable and that luteolin 5-methyl ether appears to be replaced by 7, 3′, 4′-trihydroxyflavone. In addition, the aurone aureusidin is more commonly present than in the leaves and is occasionally accompanied by two further aurones. The glycoxanthones mangiferin and isomangiferin occur rarely in all three species examined in the section *Haspani*, i.e. in *C. haspan*, *C. prolifer* and *C. tenuispica*. In general, however, the flavonoid data do not offer any markers which separate off different sections within the genus; there are, however, some significant correlations between the frequency of the flavonoid classes and subgeneric groupings.

INTRODUCTION

Previous surveys of flavonoids in the Cyperaceae have established that this family has a distinctive pattern of constituents in leaf, fruit and inflorescence [1–3]. Leaf flavonoids are mainly flavone-based (luteolin, tricin and flavone *C*-glycosides) with flavonols occurring in only *ca* 11% of the species so far examined [2, 3]. Fruit and inflorescences are coloured due to the presence of the aurone aureusidin, together with the characteristic 3-desoxyanthocyanidin carexidin [1]. In addition, earlier work suggested that the leaf flavonoids are correlated in their distribution with plant geography. In particular, certain compounds such as luteolin 5-methyl ether and 6-hydroxyluteolin were confined to African and South American taxa only [3].

Although Cyperaceae is well represented in the Australian flora, only a few such species were surveyed earlier. In order to see if the correlation between chemistry and plant geography extends to Australian taxa, a study has now been initiated of the Cyperaceae of Australasia. The present paper is concerned with the flavonoids of those plants usually included in *Cyperus*, the type genus of the family. This study has coincided with a taxonomic revision of the genus being carried out by one of us (K.L.W.) so that freshly collected and authenticated specimens were available for phytochemical analysis (Table 1). Most species sampled are native to Australia but introduced species have been included where available. There are considerable difficulties in the classification of sedges and an additional reason for this survey was to seek new characters for delimiting sectional and subgeneric groupings. For present purposes, the species are arranged (Table 1) in subgenera and sections largely according to Kükenthal [4], with some name changes from Kern [5] and some rearrangement of species following morphological studies [Wilson, K. L., unpublished results].

RESULTS

Leaves and inflorescences (with or without fruits) were separated before analysis. Flavonoids were then surveyed by standard procedures in direct and hydrolysed extracts. These identifications were supported by detailed investigations of representative individual species as outlined below. The main results are shown in Table 2 for the leaves and Table 3 for the inflorescences. These results are conveniently discussed according to the major flavonoid types present.

Aurones

The yellow aurone pigments are the most distinctive flavonoid features of the Cyperaceae, since

Table 1. Classification and sources of *Cyperus* species

Subgenus, section and species	Australian source	Zonal range and distribution (outside Australia)†
ANOSPORUM		
Luzuloidei		
C. eragrostis Lam.*	K. L. Wilson 3110 Liverpool, N.S.W.	S/Te
C. reflexus Vahl.*	R. Coveny 5472 Woodford, N.S.W.	N. & S. America
Diffusi		
C. albostriatus Schrad.	K. L. Wilson 4383 Roy. Bot. Gdn., Sydney	S/Te S. Africa
C. disjunctus C. B. Clarke	R. Coveny 9877 & L. Haegi Ellenborough Falls, N.S.W.	S
C. tetraphyllus R. Br.	K. L. Wilson 3134 Whian Whian State Forest, N.S.W.	S
Pseudanosporum		
C. platystylis R. Br.	K. L. Wilson 2381 & P. Sharpe Lake Clarendon, Queensland	Tr Asia
Alternifolii		
C. gymnocaulos Steud. (a)	F. T. Turvey NSW 62519 Musgrave Range, S.A.	
C. gymnocaulos (b)	M. G. Corrick 6435 Lake Albacutya, Victoria	S/Te/E
C. gymnocaulos (c)	J. Everett 345 and S. Jacobs, Lake Tooim, Victoria	
C. involucratus Rottb.*	K. L. Wilson 4384, Roy. Bot. Gdn., Sydney	Tr/S Africa
C. vaginatus R. Br.	K. L. Wilson 839, L. Johnson & S. Jacobs, Moonbi Range, N.S.W.	S/Te/E
Haspani		
C. haspan L.	K. L. Wilson 3138 Near Lennox Head, N.S.W.	Tr/S Worldwide
C. prolifer Lam.*	K. L. Wilson 4382 Roy. Bot. Gdn., Sydney	Tr/S E. Africa
C. tenuispica Steud.	R. Carolin 8717 Near Normanton, Queensland	Tr/S Africa, Asia
Fusci		
C. concinnus R.Br.	P. K. Latz 5155 North Wauchope, N.T.	S/Te
C. difformis L. (a)	K. L. Wilson 3111 Liverpool Showground, N.S.W.	Tr/S/E
C. difformis (b)	W. B. Cox NSW 62501 Griffith, N.S.W.	Africa, Asia
Graciles		
C. aquatilis R.Br. (a)	S. Jacobs 2532 & A. Rodd Near Lowmead, Queensland	Tr/S New Guinea
C. aquatilis (b) (vel. sp. aff.)	P. Hind 509 Cape York Pen., Queensland	—
C. breviculmis R.Br.	S. Jacobs 3779 Katherine Gorge, N.T.	Tr
C. flaccidus R.Br.	K. L. Wilson 3303 Near Nepean River, N.S.W.	Tr/S
C. gracilis R.Br.	K. L. Wilson 3310 Denistone, N.S.W.	S New Caledonia
C. imbecillis R.Br.	K. L. Wilson 3135 Whian Whian State Forest, N.S.W.	S
C. laevis R.Br.	K. L. Wilson 3308 Denistone, N.S.W.	S

Table 1 (*Contd*)

Subgenus, section and species	Australian source	Zonal range and distribution (outside Australia)†
C. mirus C. B. Clarke	K. L. Wilson 3136 Whian Whian State Forest, N.S.W.	S
C. stradbrokensis Domin	K. L. Wilson 3141 Near Lennox Head, N.S.W.	S
Tenelli		
C. tenellus L. fil.*	J. H. Willis Langwarrin, Victoria	Te S. Africa
CYPERUS		
Papyri		
C. papyrus L.*	K. L. Wilson 4381, Roy. Bot. Gdn., Sydney	Tr/S Africa
Exaltati		
C. alopecuroides Rottb.	P. Sharpe 1546 Rita Island, Queensland	Tr Worldwide
C. exaltatus Retz.	K. L. Wilson 2366 SW of Garah, N.S.W.	Tr/S Africa, Asia
Rotundi		
C. bifax C. B. Clarke	K. L. Wilson 1869 Near Mungindi, N.S.W.	Tr/S/E Africa, Asia
C. rotundus L.*	K. L. Wilson 3309 Denistone, N.S.W.	Tr/S/E Worldwide
C. victoriensis C. B. Clarke	R. Coveny 2540 Near Forbes, N.S.W.	S/E
Bulbosi		
C. bulbosus Vahl	P. L. Milthorpe & G. M. Cunningham 5166 Clifton Downs, N.S.W.	Tr/E Africa, Asia
Subimbricati		
C. sphacelatus Rottb.*	P. Sharpe 2328 & J. Elsol Near Nambour, Queensland	Tr Africa, C. & S. America
C. tenuiculmis Boeck.	P. R. Sharpe 2152 Peregian, Queensland	Tr Africa, Asia
Distantes		
C. distans L. fil.	P. Sharpe 1465 Cairns, Queensland	Tr/S Worldwide
Proceri		
C. pilosus Vahl	K. L. Wilson 3138 Near Lennox Head, N.S.W.	Tr/S Africa, Asia
C. procerus Rottb.	K. L. Wilson 3324, Bruce Highway, 3 km S. of Six Mile Creek, Queensland	Tr/S Asia
Iriae		
C. iria L. (a)	G. M. Cunningham 4650 & P. L. Milthorpe Miandetta, N.S.W.	Tr/S/E Africa, Asia
C. iria (b)	K. Brennan NSW 145685 Kununurra, W.A.	—
Compressi		
C. compressus L.	P. Sharpe 1573 Near Mackay, Queensland	Tr Worldwide
Amabiles		
C. castaneus Willd. (a) var. *castaneus*	R. Carolin 8355 Charters Towers, Queensland	Tr/S Asia
C. castaneus Willd. (b) var. *brevimucronatus* Kük.	P. K. Latz 6944 Murray Downs Station, N.T.	Tr/E
C. castaneus Willd. (c) var. *nov*?	Lazarides & Adams 114 Maranboy Police Station, N.T.	Tr
C. cuspidatus H. B. K. (a)	C. R. Dunlop 5273 Mitchell River, W.A.	Tr Worldwide

Table 1 (*Contd*)

Subgenus, section and species	Australian source	Zonal range and distribution (outside Australia)†
C. cuspidatus (b)	K. L. Wilson 3888 & P. Sharpe, 15.5 km N.E. of Gin Gin Rd., Queensland	—
Dichostylis		
C. pygmaeus Rottb.	K. L. Wilson 1745 Near Weemelah, N.S.W.	Tr/S/E Africa, Asia
Laevigati		
C. laevigatus L.	K. L. Wilson 3306 Kurnell, N.S.W.	Tr/S/Te/E Worldwide
C. laevigatus 'form 1'	A. C. Beauglehole 28111 Near Williams Creek, S.A.	—
C. laevigatus 'form 2'	K. L. Wilson 1640 & J. Pickard, Near Moalie Park Homestead, N.S.W.	—
PYCREUS		
Chrysanthi		
C. unioloides R.Br.	R. Coveny 10604 & P. Hind Barcoongere State Forest, N.S.W.	Tr Worldwide
Globosi		
C. flavidus Retz.	J. O'Hara & R. Coveny 3517 Near Yamba, N.S.W.	Tr/S Africa, Asia
Albomarginati		
C. macrostachyos Lam.	K. Brennan NSW 62500 Kununurra, W.A.	Tr Africa, N. & C. America
Pycreus		
C. polystachyos Rottb.	K. L. Wilson 3137 Near Lennox Head, N.S.W.	Tr/S Worldwide
C. sulcinux C. B. Clarke	S. T. Blake 23259 Cooktown, Queensland	Tr Asia
Pumili		
C. nervulosus (Kük.) S. T. Blake	P. K. Latz 6923 Davenport Range, N.T.	Tr/E New Guinea
C. pumilus L.	S. Jacobs 3731 Near Darwin, N.T.	Tr Asia
Vestiti		
C. sanguinolentus Vahl	K. L. Wilson 3130 Whian Whian State Forest, N.S.W.	Tr/S/Te Africa, Asia
Flavescentes		
C. flavescens L.	K. L. Wilson 3129 Whian Whian State Forest, N.S.W.	S/Te Europe, Africa, America
MARISCUS		
Strigosi		
C. bowmanii Benth.	S. T. Blake 12925 Brisbane, Queensland	S
C. leiocaulon Benth.	K. L. Wilson 3140 Near Lennox Head, N.S.W.	S
C. scaber (R.Br.) Boeck.	R. Coveny 2016 North Stradbroke Island, Queensland	Tr/S
Subulati		
C. subulatus R.Br.	R. Coveny 9312 Red Rock, N.S.W.	S
Thunbergiani		
C. congestus Vahl (a)*	K. L. Wilson 3311 Boronia Park, N.S.W.	S/Te Africa

Table 1 (*Contd*)

Subgenus, section and species	Australian source	Zonal range and distribution (outside Australia)†
C. congestus (b)*	K. L. Wilson 2160 Mouth of Snowy River, Victoria	—
C. lucidus R.Br.	R. Coveny 5053 Billinudgel, N.S.W.	Tr/S/Te New Guinea, Norfolk Is.
C. rigens Presl*	K. L. Wilson 3305 Lawson, N.S.W.	Tr S. America
Pinnati		
C. betchei (Kük.) (a) S. T. Blake	S. T. Blake 19155 Cypress Downs, Queensland	S
C. betchei (b)	R. Coveny 8664 & S. K. Roy Near Narrabri, N.S.W.	—
C. betchei (c)	R. Melville 3444 Near Jackson, Queensland	—
C. carinatus R.Br.	P. K. Latz 5176 N. of Tennant Creek, N.T.	Tr
C. clarus S. T. Blake	S. T. Blake 5174 Drayton, Queensland	S
C. cunninghamii (C. B. Clarke) C. A. Gardner	A. A. Mitchell 453 Belvedere Copper Mine, Wyloo Homestead, W.A.	Tr/E
C. sp. aff. *cunninghamii* (a)	P. K. Latz 2012 Mt. Doreen Station, N.T.	E
C. sp. aff. *cunninghamii* (b)	P. K. Latz 7565 Haast Bluff Station, N.T.	E
C. sp. aff. *cunninghamii* (c)	P. K. Latz 5444 Ord River Dam, W.A.	E
C. dactylotes Benth. (a)	P. K. Latz 6915 Murray Downs Station, N.T.	Tr/E
C. dactylotes (b)	K. Wilson 3415 & P. Sharpe 3 km E. of Wallumbilla, Queensland	Tr/E
C. fulvus R.Br. (a)	K. L. Wilson 1770 Goondabluie, N.S.W.	Tr/S New Guinea
C. fulvus R.Br. (b)	K. L. Wilson 2368 SW of Garah, N.S.W.	Tr/S New Guinea
C. gilesii Benth.	B. G. Briggs 5409 & J. Seur Near Tibooburra, N.S.W.	S/E
C. gunnii Hook.f.	K. L. Wilson 1380 Dunmore State Forest Road, Queensland	Tr/S/Te
C. holoschoenus R.Br.	K. Brennan NSW 145686 Kununurra, W.A.	Tr New Guinea
C. ixiocarpus F. Muell.	D. E. Symon 10083 Near Port Hedland, W.A.	Tr/E
C. lhotskyanus Boeck.	A. C. Beauglehole 63100 Lake Jollicum Wild Life Reserve, Victoria	S/Te
C. perangustus S. T. Blake	K. L. Wilson, 3670 & P. Sharpe, Yippoon, Queensland	Tr/S
C. portae-tartari K. L. Wilson	C. R. Dunlop 5369 Mitchell River, W. A.	Tr
C. rigidellus (Benth.) (a) J. M. Black	P. K. Latz 5016 Mulga Park Station, N.T.	S/E
C. rigidellus (b)	A. C. Beauglehole 56179 Robinvale, Victoria	S
C. rigidellus (c)	K. L. Wilson 1634 McCallum Park, N.S.W.	S
C. rigidellus (d)	K. L. Wilson 2006 Near Garah, N.S.W.	S

Table 1 (*Contd*)

Subgenus, section and species	Australian source	Zonal range and distribution (outside Australia)†
C. sp. aff. *rigidellus*	R. Coveny 8881 & S. K. Roy Mt. Kaputar National Park, N.S.W.	S
C. sexflorus R.Br.	P. K. Latz 1406 Tanumbirini Waterhole, N.T.	Tr
C. sporobolus R.Br.	C. Dunlop 4069 Hayes Creek, N.T.	Tr
C. viscidulus K. L. Wilson	C. R. Dunlop 5231 Mitchell River, W.A.	Tr
C. sp. B.	P. K. Latz 2200 Kurundi Station, N.T.	Tr/E
C. sp. L.	P. K. Latz 5372 Farquharsen Gap, N.T.	Tr
C. sp. S.	S. T. Blake 16035 38 km NW of Katherine, N.T.	Tr
Pennati		
C. conicus (R.Br.) Boeck.	P. K. Latz 5156 Tennant Creek, N.T.	Tr/S/E
C. javanicus Houtt.	S. T. Blake 14520 Trinity Beach, Queensland	Tr Pacific Is., Africa, Asia
Aristati		
C. squarrosus L.	S. T. Blake 14020 Noondoo, Queensland	Tr/S/E Worldwide
Mariscus		
C. cyperinus (Retz.) Suring.	S. T. Blake 19729 Daintree, Queensland	Tr Asia, Pacific Is.
C. cyperoides (L.) O. Kuntze	L. A. S. Johnson 7515 Near Kenpsey, N.S.W.	Tr/S Africa, Asia
C. flavus (Vahl) Nees*	S. Jacobs N.S.W. 144403 Carlton, N.S.W.	Tr/S C. & S. America
KYLLINGA		
Kyllinga		
C. brevifolius (Rottb.) Hassk. (a)	K. L. Wilson 3313 Boronia Park, N.S.W.	Tr/S/Te Worldwide
C. brevifolius (b)	K. L. Wilson 3302 Balmain, N.S.W.	—
C. sesquiflorus (Torr.) Mattf. & Kük.	K. L. Wilson 3312 Boronia Park, N.S.W.	Tr/S Worldwide
TORULINIUM		
C. odoratus L.	P. Sharpe 1554 Cairns, Queensland	Tr/S Worldwide
REMIREA		
C. pedunculatus (R.Br.) Kern	C. Dunlop 3443 Melville Island, N.T.	Tr/S Worldwide

*Introduced species.

†Tr, tropical; S, subtropical; Te, temperate; E, eremaean arid zone (of Australia only). All distributions are approximate and the division between subtropical and temperate is not always clear cut.

possession of the aurone character marks the family off from all other monocotyledonous groups. Aureusidin (4, 6, 3′, 4′-tetrahydroxyaurone) was previously recorded in fruits of *Lepironia, Eleocharis, Scirpus, Schoenus, Gahnia* and *Ptilanthelium* species [1]. The only previous records in *Cyperus* were in the fruits of *C. rotundus* and *C. pedunculatus* (*Remirea maritima*) [1]. Aureusidin has now been detected in inflorescences of over 55% of the *Cyperus* taxa surveyed. It sometimes occurs in high concentration (e.g. in *C. conicus, C. gilesii, C. gunnii*) and in such cases almost certainly contributes to the golden brown pigmentation of the inflorescence.

Aureusidin is accompanied (or replaced) in some 18 species all native to Australia by a second aurone, called for convenience mariscetin. It has not yet been fully characterized but from R_f data appears to be more highly hydroxylated than aureusidin. The R_f

Table 2. The distribution of flavonoid aglycones in leaves of Australian *Cyperus* species

Species	Flavones	Flavonols	Procyanidin	Aurones
ANOSPORUM				
Luzuloidei				
C. eragrostis	Tr, Lu	Flavonol methyl ethers	+	—
C. reflexus	Tr, Lu, Lu 5ME	—	(+)	—
Diffusi				
C. albostriatus	Tr, Lu	—	+	—
C. disjunctus	Lu5ME?	—	—	—
C. tetraphyllus	Lu	Qu 3ME, Km 3ME	too weak	—
Pseudanosporum				
C. platystylis	Tr, Lu*	—	(+)	Au
Alternifolii				
C. gymnocaulos (a)	Tr, Lu	—	—	(Au)
C. gymnocaulos (b)	(Tr) Lu	—	—	Au
C. gymnocaulos (c)	Lu	—	+	Au
C. involucratus	(Tr) Lu*	—	+	Au
C. vaginatus	(Tr) Lu	—	—	Au
Haspani				
C. haspan§	—	Qu	+	—
C. prolifer	—	Qu	+	Au
C. tenuispica	—	Qu	—	Au
Fusci				
C. concinnus	Tr, Lu	—	+	—
C. difformis (a)	Lu		too weak	
C. difformis (b)	Tr, Lu	—	—	—
Graciles				
C. aquatilis (a)	Lu5ME?	Qu	—	—
C. aquatilis (b)	(Lu5ME?)	(Qu)	—	—
C. breviculmis	—	(Qu)	—	(Au)
C. flaccidus	Lu, Lu5ME	Qu	+	—
C. gracilis	Tr, Lu	—	+	—
C. imbecillis	Tr, Lu	—	+	—
C. leavis	Tr, Lu	(Qu)	+	—
C. mirus	Lu‡		too weak	
C. stradbrokensis	Tr, Lu	Flavonol methyl ethers?	+	—
Tenelli				
C. tenellus	Tr	—	(+)	—
CYPERUS				
Papyri				
C. papyrus	Lu	—	(+)	—
Exalta				
C. alopecuroides	Tr*	—	—	—
C. exaltatus	Tr*	—	+	—
Rotundi				
C. bifax	Tr, Lu‡	—	—	—
C. rotundus	Lu	—	—	—
C. victoriensis	Tr, Lu	—	—	—
Bulbosi				
C. bulbosus	Tr, Lu, Ap‡	—	—	—
Subimbricati				
C. sphacelatus	Tr, Lu	—	—	—
C. tenuiculmis	Tr, Lu? Lu5ME	Qu?	+	Au
Distantes				
C. distans	Tr, Lu	—	—	—

Table 2 (*Contd*)

Species	Flavones	Flavonols	Procyanidin	Aurones
Proceri				
C. pilosus	Tr, Lu	—	—	—
C. procerus	Tr, Lu	—	+	—
Iriae				
C. iria (a)	Tr	—	—	Au
C. iria (b)	Tr, Lu	—	—	(Au)
Compressi				
C. compressus	Tr, Lu, Ap, Lu5ME	—	—	—
Amabiles				
C. castaneus (a) var. *castaneus*	Tr, Lu, Ap	—	—	—
C. castaneus (b) var. *brevimucronatus*	Tr, Lu	—	+	—
C. castaneus (c) var. *nov.*	Tr, Lu, Ap	—	—	—
C. cuspidatus (a)	(Tr), Lu, (Ap)	—	(+)	—
C. cuspidatus (b)	Lu, Ap	—	+	+
Dichostylis				
C. pygmaeus	Tr, Lu	—	+	—
Laevigati				
C. laevigatus	Tr, Lu,‡ Lu5ME	—	—	(+)
C. laevigatus 'form 1'	Tr, Lu‡	—	—	—
C. laevigatus 'form 2'	Tr, Lu	—	—	—
PYCREUS				
Chrysanthi				
C. unioloides	Tr, Lu	—	—	—
Globosi				
C. flavidus	Tr, Lu	—	+	—
Albomarginati				
C. macrostachyos	Tr, Lu	—	—	Au
Pycreus				
C. polystachyos	Tr, Lu, Lu5ME‡	—	—	—
C. sulcinux	Tr, Lu, Ap	—	—	—
Pumili				
C. nervulosus	Lu, Ap	—	—	—
C. pumilus	(Tr)?		too weak	—
Vestiti				
C. sanguinolentus	Tr, Lu, Lu5ME‡	Flavonol methyl ethers?	+	—
Flavescentes				
C. flavescens	Tr, Lu, Lu5ME‡	—	—	—
MARISCUS				
Strigosi				
C. bowmanii	Tr, Lu, Ap	—	—	—
C. leiocaulon	Tr, Lu‡	Flavonol methyl ethers	+	—
C. scaber	(Tr), Lu	—	—	Au
Subulati				
C. subulatus	Tr, Lu (Lu5ME)‡	—	—	—

Table 2 (*Contd*)

Species	Flavones	Flavonols	Procyanidin	Aurones
Thunbergiani				
C. congestus (a)	Tr, Lu	—	+	—
C. congestus (b)	Lu	Flavonol methyl ethers?	—	(Au)
C. lucidus	Lu, Lu5ME	—	(+)	Au
C. rigens	Tr, Lu	—	+	—
Pinnati				
C. betchei (a)	Tr, Lu	—	—	—
C. betchei (b)	Tr, Lu	—	—	Au
C. betchei (c)	(Tr), Lu	Flavonol methyl ethers		(Au)
C. carinatus	Tr, Lu	—	+	Au
C. clarus	Tr, Lu	—	—	—
C. cunninghamii	Tr, Lu†	Qu3ME, Km3ME, Km 3, 7-diME	—	—
C. sp. aff. *cunninghamii* (a)	Tr, Lu†	Qu3ME, Km3ME	—	Au
C. sp. aff. *cunninghamii* (b)	Tr, Lu†	—	+	Au
C. sp. aff. *cunninghamii* (c)	too weak		+	Au
C. dactylotes (a) and (b)	Lu	Qu3ME, Qu3, 7-diME, Qu3, 7, 3′-triME?, Km 3ME, Km 3, 7-diME	+	Au
C. fulvus (a)	Tr, Lu	—	(+)	Au
C. fulvus (b)	Tr, Lu	—	+	Au
C. gilesii	Tr, Lu	—	—	Au
C. gunnii	Tr, Lu	Flavonol methyl ethers?	(+)	Au
C. holoschoenus	Tr	—	—	Au
C. ixiocarpus	Tr, Lu	—	+	—
C. lhotskyanus	Tr, Lu	—	+	—
C. perangustus	(Tr), Lu, (Ap)	Flavonol methyl ethers	+	Au
C. portae-tartari	Tr, Lu	—	(+)	Au
C. rigidellus (a)	Lu	Qu 3ME, Qu 3, 7-diME, Qu 3, 7, 3′-triME	—	Au
C. rigidellus (b)	Tr, Lu	Flavonol methyl ethers	+	Au
C. rigidellus (c)	Lu	Qu 3ME, Qu 3, 7-diME, Qu 3, 7, 3′-triME or Km 3, 7-diME	+	Au
C. rigidellus (d)	Tr, Lu	—	+	Au
C. sp. aff. *rigidellus*	Lu	—	+	Au
C. sexflorus	Lu	Km 3ME	—	Au
C. sporobolus	(Lu)	—	—	Au
C. viscidulus	Tr, Lu	—	+	Au
Cyperus sp. B	Lu	Qu 3ME, (Qu 3, 7-diME), Qu 3, 7,3′-triME?, Km 3ME	+	—
Cyperus sp. L	Lu	—	+	Au
Cyperus sp. S	Tr, Lu	—	—	Au
Pennati				
C. conicus	Tr, Lu†	—	+	Au
C. javanicus	Tr, Lu	—	—	Au
Aristati				
C. squarrosus	—	Qu	—	Au
Mariscus				
C. cyperinus	Lu, Lu5ME	—	—	—
C. cyperoides	Tr, Lu	—	—	—
C. flavus	Tr, Lu‡	—	+	—

Table 2 (*Contd*)

Species	Flavones	Flavonols	Procyanidin	Aurones
KYLLINGA				
Kyllinga				
C. brevifolius (a)	Tr‡	—	+	—
C. brevifolius (b)	(Tr)‡	(Qu)	+	—
C. sesquiflorus		Too weak		
TORULINIUM				
C. odoratus	Tr, Lu	—	+	—
REMIREA				
C. pedunculatus	Tr, Lu	—	+	—

Key: Tr, tricin; Lu, luteolin; Lu5ME, luteolin 5-methyl ether; Ap, apigenin; Qu, quercetin; Qu 3ME, quercetin 3-methyl ether; Qu 3, 7-diME, quercetin 3, 7-dimethyl ether; Qu 3, 7, 3′-triME, quercetin 3, 7, 3′-trimethyl ether; Km 3ME, kaempferol 3-methyl ether; Km 3, 7-diME, kaempferol 3, 7-dimethyl ether; Au, aureusidin; ( ), trace constituent.

*Flavone *C*-glycosides present.

†Flavone *C*-glycosides may possibly be present.

‡Sulphated flavones present.

§Mangiferin and isomangiferin present.

Table 3. The distribution of flavonoid aglycones in the inflorescences of Australian *Cyperus* species

Species	Flavones	Flavonols	Aurones
ANOSPORUM			
Luzuloidei			
C. eragrostis	—	—	—
C. reflexus	7, 3′, 4′-TriOH	Qu	Au, Am
Diffusi			
C. albostriatus	*C*-glycosides (?)	—	—
C. disjunctus	—	—	—
C. tetraphyllus	Lu	—	Au
Pseudanosporum			
C. platystylis	—	—	Au
Alternifolii			
C. gymnocaulos (a)	Lu	—	Au
C. gymnocaulos (b)	—	—	Au
C. gymnocaulos (c)	Lu	—	Au
C. involucratus	—	—	(Au)
C. vaginatus	Lu	—	Au
Haspani			
C. haspan†	—	—	—
C. prolifer†	—	—	Au
C. tenuispica†	—	—	—
Fusci			
C. concinnus	Lu	—	—
C. difformis (a)	Lu	—	—
C. difformis (b)	Lu	—	Au
Graciles			
C. aquatilis (a)	—	Qu	—
C. aquatilis (b)	—	Qu	—
C. breviculmis	—	Qu	—
C. flaccidus	—	Qu	—
C. gracilis	—	—	—
C. imbecillis	—	—	—
C. laevis	—	—	—
C. mirus	—	—	Au
C. stradbrokensis	Lu	—	—

Table 3 (Contd)

Species	Flavones	Flavonols	Aurones
Tenelli			
C. tenellus	—	—	—
CYPERUS			
Papyri			
C. papyrus	Lu	Qu	Au
Exaltati			
C. alopecuroides	Lu	—	Au
C. exaltatus	Lu	—	Au
Rotundi			
C. bifax	Lu	—	Au
C. rotundus	Lu	—	Au
C. victoriensis	Lu	—	Au
Bulbosi			
C. bulbosus	Lu	—	Au, Mt
Subimbricati			
C. sphacelatus	Lu	—	—
C. tenuiculmis	Lu	—	Au, Mt
Distantes			
C. distans	Lu, 7, 3', 4'-TriOH	—	Au
Proceri			
C. pilosus	Lu	—	—
C. procerus	Lu	—	—
Iriae			
C. iria (a)	Lu	—	Au, Mt
C. iria (b)	Lu*	Qu	Au, Mt
Compressi			
C. compressus	Lu*	—	Au
Amabiles			
C. castaneus (a) var. *castaneus*	Lu	—	Au
C. castaneus (b) var. *brevimucronatus*	Lu	—	Au
C. castaneus (c) var. nov.	Lu	—	Au
C. cuspidatus (a)	Lu	—	Au
C. cuspidatus (b)	Lu, Ap	—	Au
Dichostylis			
C. pygmaeus	Lu*	—	—
Laevigati			
C. laevigatus	Lu, 7, 3', 4'-TriOH	—	Au
C. laevigatus 'form 1'	Lu	—	—
C. laevigatus 'form 2'	Lu	—	—
PYCREUS			
Chrysanthi			
C. unioloides	Lu	—	—
Globosi			
C. flavidus	Lu	—	—
Albomarginati			
C. macrostachyos	Lu	—	Au
Pycreus			
C. polystachyos	Lu	—	—
C. sulcinux	Lu	—	—
Pumili			
C. nervulosus	Lu, Ap	—	—
C. pumilis	Lu	—	—
Vestiti			
C. sanguinolentus	Lu	—	—
Flavescentes			
C. flavescens	Lu	—	—

Table 3 (*Contd*)

Species	Flavones	Flavonols	Aurones
MARISCUS			
Strigosi			
C. bowmanii	Lu	—	Au, Mt
C. leiocaulon	Lu	—	Mt
C. scaber	Lu	—	Au, Mt
Subulati			
C. subulatus	—	—	—
Thunbergiani			
C. congestus (a)	Flavone *C*-glycoside?	—	—
C. congestus (b)	Lu	—	Au
C. lucidus	Lu	—	Au
C. rigens	Lu	—	Au
Pinnati			
C. betchei (a)	Lu, 7, 3′, 4′-TriOH	—	Mt
C. betchei (b)	Lu	—	Au, Mt
C. betchei (c)	7, 3′, 4′-TriOH	—	Au, Mt
C. carinatus	Lu, Ap	—	—
C. clarus	Lu	—	—
C. cunninghamii	Lu	—	Au
C. sp. aff. *cunninghamii* (a)	Lu	—	Au, Mt
C. sp. aff. *cunninghamii* (b)	Lu	—	Au, Mt
C. sp. aff. *cunninghamii* (c)	Lu	—	Au
C. dactylotes	Lu	—	—
C. fulvus (a)	Lu	—	—
C. fulvus (b)	Lu	—	—
C. gilesii	Lu	—	Au, Mt
C. gunnii	Lu	—	Au, Mt
C. holoschoenus	—	—	—
C. ixiocarpus	Lu	—	Mt
C. lhotskyanus	Lu 7, 3′, 4′-TriOH	—	Au
C. perangustus	—	—	Au, Mt
C. portae-tartari	—	—	Au, Mt
C. rigidellus (a)	Lu	—	Au
C. rigidellus (b)	Lu 7, 3′, 4′-TriOH	—	Au
C. rigidellus (c)	Lu	—	Au
C. rigidellus (d)	—	—	Au
C. sp. aff. *rigidellus*	7, 3′, 4′-TriOH	—	—
C. sexflorus	Lu	—	Au
C. sporobolus	Lu	—	Au
C. viscidulus	Lu	—	Au
Cyperus sp. B	Lu	—	—
Cyperus sp. L	Lu	—	Au, Mt
Cyperus sp. S	Lu	—	Au
Pennati			
C. conicus	Lu	—	Au, Mt
C. javanicus	—	—	—
Aristati			
C. squarrosus	—	Qu	Au, Mt
Mariscus			
C. cyperinus	Lu	—	—
C. cyperoides	Lu	—	—
C. flavus	Lu	—	—
KYLLINGA			
Kyllinga			
C. brevifolius (a)	Lu	—	—
C. brevifolius (b)	—	—	—
C. sesquiflorus	—	—	—
TORULINIUM			
C. odoratus	Lu	—	Au

Table 3 (*Contd*)

Species	Flavones	Flavonols	Aurones
REMIREA			
C. pedunculatus	Lu	—	Au

Key: 7, 3′, 4′-TriOH, 7, 3′, 4′-trihydroxyflavone; Lu, luteolin; Ap, apigenin; Qu, quercetin; Au, aureusidin; Am, aurone methyl ether; Mt, mariscetin; ( ) = trace constituent.

*Sulphated flavones present.

†Mangiferin and isomangiferin present.

and spectral properties suggest it could be the so far undescribed 7-hydroxy derivative of aureusidin; it is different from the known bracteatin (4, 6, 3′, 4′, 5′-pentahydroxyaurone) which was available for comparison. A second new aurone was also detected in fruit of *C. reflexus*, a species native to America which from its relatively high R_f values, was assumed to be a methyl ether, but again it needs further examination. It was clearly different from leptosidin (6, 3′, 4′-trihydroxy-7-methoxyaurone), which has very recently been reported as the 6-glucosylrhamnoside in the leaves of an Asian *Cyperus* species, *C. scariosus* [6]. Examination of other species in the American section luzuloidei would be of interest.

Previously, aureusidin was recorded in Cyperaceae only in the free state. In the present work, it was found to occur always as such, but in addition a glycosidic form was also apparent in a number of species. This appears to be the 6-glucoside, aureusin, since this was isolated and characterized from at least one species. The new aurone mariscetin also occurs both free and in glycosidic form. The present discovery of aureusidin in inflorescences of most Australian *Cyperus* species surveyed suggested that an examination of European *Cyperus* species would be of interest. Indeed, aureusidin was detected in 8 of 16 species examined [Harborne, J. B., unpublished results], so that further studies of European taxa are being pursued.

While aurones occur characteristically in inflorescences of *Cyperus*, they can also be detected, usually in lesser amounts, in other tissues. During the present survey, they were found in leaves of *ca* 38% of the Australian *Cyperus* species (Table 2). While aureusidin was the most usual component, the two new aurones noted in the inflorescences (see above) were also occasionally present.

Flavones

The flavones tricin and luteolin, present as *O*-glycosides, and *C*-glycosylflavones have been recorded previously in *Cyperus* leaves, but only a few taxa were then examined [2, 3]. The present survey (Table 2) represents the widest examination of the genus so far and confirms that tricin and luteolin are nearly universal in their occurrence. They are usually present in glycosidic form and, from 2-D chromatograms of leaf extracts, it was apparent that a variety of glycosides are present. These have been examined in a few species and 10 derivatives of luteolin, luteolin 5-methyl ether and tricin have been identified (Table 4).

It appears from 2-D chromatograms that luteolin and tricin commonly occur in *Cyperus* as the 7-glucosides and/or 7-glucuronides. Other forms are regularly present (e.g. various 7-diglycosides yet to be characterized) and occasionally anionic sulphated compounds are present. In particular, several sulphated forms of tricin were noted variously in *C. flavus*, *C. leiocaulon*, *C. mirus*, *C. polystachyos* and *C. sanguinolentus* (Table 4). Although tricin 7-glucosidesulphate has been recorded previously in members of the Palmae [7], the two tricin 7-glucuronidesulphates appear to be novel. These compounds could only be provisionally characterized since further studies are needed to determine the position of attachment of the sulphate moieties. The parent tricin 7-sulphate was synthesized for comparison (see Experimental) but was not detected as such in any of these plants.

One other flavone, luteolin 5-methyl ether, was found in the leaves in 12% of the taxa surveyed (Table 2). Its identity was confirmed in several species but, due to lack of material, it could not be confirmed in all cases. It is probably present in combined form as the 7-glucoside and this compound was identified in one case, in *C. flavescens*. While luteolin 5-methyl ether has been recorded in leaves of African and South American Cyperaceae [3], this is the first record of it in Australian taxa and also in the genus *Cyperus*.

Glycoflavones were notable during this survey by their general absence. They were positively identified in three species and provisionally noted as being possibly present in three further taxa (Table 2). On this evidence, they appear to be rare in the genus *Cyperus*. This contrasts with their widespread occurrence in the family as a whole, their general frequency of occurrence being 67%.

Flavone *O*-glycosides (but not *C*-glycoflavones) are also commonly present in inflorescences of *Cyperus* species (Table 3). Only one aglycone, luteolin, was regularly present. Tricin, so common in the leaves, appeared to be completely absent. Apigenin was rarely present, accompanying luteolin in two species *C. carinatus* and *C. nervulosus*. As with the leaves, the flavones of the inflorescences appear to be commonly present as the 7-glucoside and/or 7-glucuronide. Such glycosides were positively identified from a few representative species (Table 4).

A blue-fluorescing flavone with similar properties in UV light as luteolin 5-methyl ether was found in the inflorescence of several *Cyperus* species (Table 3). In two cases further examined [*C. rigidellus* (b), *C.* sp.

Table 4. Flavonoid conjugates identified in *Cyperus*

Flavonoid conjugate	Identified in
Apigenin	
7-glucoside	*C. carinatus*†
7-glucuronide	*C. carinatus*†
Luteolin	
7-glucoside	*C. carinatus*,*† *C. flavus*,* *C. pilosus*†
7-glucuronide	*C. cunninghamii*,* *C. flavescens*,* *C. flavus*,* *C. leiocaulon*,† *C. polystachyos*†
Luteolin 5-methyl ether	
7-glucoside	*C. flavescens**
Tricin	
7-glucoside	*C. cunninghamii*,* *C. flavus**
7-glucuronide	*C. cunninghamii*,* *C. flavescens*,* *C. flavus**
7-glucosidesulphate	*C. flavus*,* *C. leiocaulon*,* *C. sanguinolentus**
7-glucosidedisulphate	*C. leiocaulon**
7-glucuronidesulphate	*C. leiocaulon*,* *C. polystachyos*,* *C. sanguinolentus**
7-glucuronidedisulphate	*C. polystachyos*,* *C. sanguinolentus**
Quercetin	
3-glucuronide	*C. haspan**

*Identified in leaf.
†Identified in inflorescence.

aff. *rigidellus*], this component was clearly different in R_f from luteolin 5-methyl ether and could be identified as 7, 3', 4'-trihydroxyflavone by direct comparison with an authentic specimen. This is the first report of a 5-deoxyflavone in the Cyperaceae, but the same compound has been reported as a rare constituent in the Juncaceae [8]. It appears to replace luteolin 5-methyl ether that is known in the leaf. In view of their close structural similarity, a vicarious distribution pattern might be expected for them but their distinctive presence in either leaf or inflorescence is exceptional.

Flavonols

Earlier surveys have indicated that the common flavonols are infrequent constituents of the Cyperaceae [3]. That this is true in the genus *Cyperus* is apparent from the present survey (Tables 2 and 3). The flavonol quercetin was only detected in leaves in 9% of the sample and in inflorescences in 6%. It probably occurs in glycosidic form; indeed quercetin 3-glucuronide was readily identified in leaves of *C. haspan* (Table 4). Kaempferol, which normally accompanies quercetin in plants, was not detected in any of the plants under examination. While some of the species with quercetin also had flavones a few, and notably four in the subgenus *Anosporum* (Table 2), were distinguished by lacking any flavone constituents.

Unhydrolysed alcoholic extracts of the leaves of a number of species showed the presence on 2-D chromatograms of a flavonoid component with a high R_f in butanol–acetic acid–water and low R_f in 15% acetic acid occupying a position usually taken up by partly methylated flavonoids. Isolation of this component on paper and fractionation by TLC revealed the presence of a mixture of up to five methylated flavonols. These were identified by spectral measurements, colour reactions and chromatographic comparison with synthetic markers as the 3-monomethyl ether, 3, 7-dimethyl ether and 3, 7, 3'-trimethyl ether of quercetin and the 3-monomethyl and 3, 7-dimethyl ether of kaempferol. One or other of these methyl ethers were positively identified in eight taxa (Table 2) and they were provisionally detected without further identification in a further eight taxa, the overall frequency being *ca* 15%. These substances were not found at all in the inflorescence extracts. Such flavonol methyl ethers are mainly found in plants in bud exudates and in wax deposits on leaves [9] and this occurrence in *Cyperus* leaves is unexpected. Such compounds have not been recorded before in the Cyperaceae and are relatively rare in the monocotyledons generally, apart from the Zingiberaceae [10].

Other phenolic constituents

Both direct and hydrolysed extracts of leaf and inflorescence showed the presence of a variety of other phenolic constituents, many of which could not be readily characterized. Proanthocyanidins were found to be relatively widespread in leaves, since cyanidin was detected regularly in acid-treated leaves (Table 2); these were not further examined. Trace amounts of cyanidin were also released occasionally from acid-treated inflorescences, indicating the presence of proanthocyanidins in these tissues too. Direct and hydrolysed extracts of the inflorescences also showed the presence of the still uncharacterized 3-deoxyanthocyanidin carexidin [1], as a natural pigment.

Two non-flavonoid phenolics frequently found in plants in association with glycoflavones are the glucoxanthones mangiferin and isomangiferin. These two compounds were readily recognized by their characteristic colour properties in *C. haspan* (leaf

and inflorescence), *C. prolifer* and *C. tenuispica* (inflorescences only) and their identities were confirmed by direct comparision with authentic markers. These two xanthones have a wide, albeit sporadic, distribution in the angiosperms [11]. They have been recorded before in a number of monocotyledonous sources, notably in the Iridaceae (e.g. *Iris*), Liliaceae (e.g. *Smilax*) and Orchidaceae (e.g. *Polystachya* (12) but this is the first report of these compounds in the Cyperaceae.

DISCUSSION

Flavonoid variations in the Cyperaceae

During the present survey, a representative sample of Australian *Cyperus* species has been analysed for leaf flavonoids so that comparisons can be made with leaf patterns of Cyperaceae from other continents. The majority of *Cyperus* in the present sample were tropical and subtropical in provenance and they can therefore be compared directly with species of *Cyperus* and Cyperaceae earlier examined from Africa and tropical and subtropical South America. It appears that the leaf pattern is basically similar. The discovery of luteolin 5-methyl ether in 12% of the Australian taxa lies between the previous characterization of this particular flavone in 33% of tropical members of the family and its recorded absence from temperate (European) members.

The absence of 6-hydroxyluteolin or related structures from the present plants is also noteworthy phytogeographically. This compound was only found previously in the South American genus *Lagenocarpus* and could not be found in African or northern temperate sedges. Its present absence also from Australian Cyperaceae may be significant and lends weight to the view that it may be restricted to *Lagenocarpus* and its relatives. Wider sampling of the South American taxa is still needed.

The present discovery of flavonol methyl ethers unique to Australian *Cyperus* may also have phytogeographical interest. It is, however, not yet clear whether this is a special feature of the genus *Cyperus* or whether it occurs in other Australian genera. Again, a wider sampling is necessary.

The present comparison of leaf and inflorescence constituents has confirmed the well-known, but not always sufficiently appreciated, fact that certain flavonoids are tissue-specific in their occurrences. The restriction of tricin to the leaf tissues in *Cyperus* is noteworthy, particularly when the closely related luteolin occurs in both leaf and inflorescence. The most interesting inflorescence flavonoids in *Cyperus* are undoubtedly the aurones and these do occur to a lesser extent in the leaves. Their distribution within the family as a whole is, however, still unclear; when more is known, it is possible that they may also turn out to be important taxonomic markers within these plants.

Flavonoid variation within Cyperus

Of the seven subgenera within *Cyperus* surveyed, most have now been sampled sufficiently for comparative purposes. Representative sampling was possible among four of the subgenera which are particularly well represented in the Australian flora and some differences in flavonoid frequencies are apparent (Table 5).

Taxonomically, the most significant differences would be those between *Anosporum* and *Cyperus*, since these two groups were originally treated as a single subgenus by Kükenthal [4]. More recently, they have been separated on the basis of their different photosynthetic pathways, the original subgenus *Cyperus* s.s. being used for the C_4 members, the new subgenus *Anosporum* being reserved for the C_3 members. Morphological differences also separate the species in these two subgenera [13]. While there is no single flavonoid character which separates them distinctly, there are clear differences in the relative frequencies of flavones, flavonols and aurones (Table 5). The other two subgenera *Pycreus* and *Mariscus* also have more or less distinctive patterns. Species in the subgenus *Mariscus* are noteworthy in having flavonol methyl ethers and often also a distinctive aurone, mariscetin, which is rare elsewhere.

Table 5. Flavonoid comparisons at subgeneric level within *Cyperus*

Subgenus	Flavonoid profile
Anosporum	Flavones uncommon in inflorescence (in 8/23 taxa)
	Flavonols present (10/23 leaf, 5/23 inflorescences)
	Aurones uncommon (6/23 leaf, 8/23 inflorescences)
Cyperus	Flavones universal (in all 21 taxa)
	Flavonols nearly absent (1 record in leaf, 1 in inflorescence)
	Aurones present in most inflorescences (15/21)
Pycreus	Flavones universal (in all 19 taxa)
	Flavonols absent
	Aurones absent (except from *C. macrostachyos*)
Mariscus	Flavonol methyl ethers in leaf (12/44)*
	Aurones common, especially mariscetin (30/44)†
	Proanthocyanidins frequent (22/44)

*Only otherwise found in three species of *Anosporum* and one of *Pycreus*.

†Mariscetin is characteristic of *Mariscus* spp. but is also present in three species of *Cyperus*.

At subgeneric level, leaf flavonoid patterns may be consistent irrespective of continental boundaries. Thus in subgenus *Pycreus*, the nine samples from the Australian flora surveyed (Table 2) show many similarities with the nine samples of the subgenus examined earlier from the African continent [3]. Thus luteolin 5-methyl ether occurs in four African and three Australian species while aurones and flavonols are rare in, or absent from, both African and Australian members. On the other hand, there are some differences in the frequency of tricin (in one African and seven Australian species) and of proanthocyanidin (in seven African and two Australian species). These data would suggest that some climatic factor, rather than plant geography *per se*, may be a major determinant in controlling flavonoid production in the leaves of these plants.

In the view of some taxonomists, one or more of the subgenera within the genus *Cyperus* (e.g. *Anosporum*, *Kyllinga*) deserve promotion to generic rank, although the morphological similarities within these taxa are quite pronounced. On balance, the flavonoid data indicate an overall similarity; chemistry thus would not support the view that any of these subgenera should be promoted to generic rank.

At the sectional level of classification, it is not generally possible to use flavonoids as markers for particular sections although, in many cases, species within a given section tend to be relatively uniform in their patterns. The presence or absence of aurone, in particular, tends to follow sectional divisions (cf. Tables 2 and 3). In addition, there are a number of ways in which the flavonoid results relate either to existing sectional classification or to more recent revision. For example, *Cyperus concinnus*, which was originally placed with *ca* 12 other species in section *Haspani*, has recently been moved on morphological grounds to the section *Fusci* [Wilson, K. L., unpublished results]. The chemical data as far as they are available support this removal in two respects. Firstly, all three species of section *Haspani* surveyed have mangiferin and isomangiferin in the inflorescence, while both samples of *C. difformis* (of section *Fusci*) and the species *C. concinnus* lack these distinctive phenolic components (Table 3). Secondly, there is a clear cut difference in leaf flavonoids, with quercetin occurring in section *Haspani* but being replaced in section *Fusci* (and also in *C. concinnus*) by luteolin and tricin.

Another example of the utility of flavonoid analysis is the case of *C. tenellus*. This species, introduced into Australia from Africa, has been considered either as a member of the section *Graciles* or as comprising a separate section *Tenellus* with two other African species not so far examined for flavonoids. While the chemical data are not decisive (Table 2), they do support the separation of *C. tenellus* based on morphological criteria into its own section, in that it, unlike section *Graciles*, has tricin as the only recognizable leaf flavone; it also lacks flavonols, which are common in other members of the section *Graciles*.

At the species level, there has not been sufficient sampling to be able to fully assess the degree of infra-specific variation in flavonoids. That this does occur is apparent from some of the examples where more than one sample of a given species has been surveyed (e.g. *C. congestus* and *C. rigidellus*, in Table 2). However, in other cases where two or more samples have been analysed, consistent results have been obtained (e.g. *C. aquatilis*, *C. gymnocaulos*), so that flavonoid patterns can be uniform within a species. In the case of *C. laevigatus*, three samples were analysed, one from a coastal habitat and the others from inland sites (Table 1). Interestingly, the coastal form differs chemically from the inland forms in having luteolin 5-methyl ether as an additional leaf flavone and in having aureusidin and 7, 3′, 4′-trihydroxyflavone in the inflorescence. The chemical results indicate heterogeneity within these plants and indeed there are morphological differences such that suggest they should be regarded as different subspecies or even different species.

EXPERIMENTAL

Plant material. Leaves and inflorescences were separately taken from freshly dried plant specimens recently collected from natural populations growing in Australia. In a few cases where leaf tissue was limited, stem tissue was included for the leaf analysis. Voucher specimens are deposited in the National Herbarium of N.S.W. under the numbers shown in Table 1.

Flavonoid analysis. General procedures were as indicated elsewhere [1–3]. Because of interference by large amounts of non-flavonoid phenolic constituents, additional methods were sometimes required to confirm the presence/absence of given flavonoid aglycones. These are indicated below. Known glycosides (Table 4) were isolated and identified by standard procedures; in all cases co-chromatography with authentic samples was carried out in at least 4 solvents.

The identification of luteolin and tricin in leaves of Cyperus *species.* Flavonoid glycosides were separated from 80% MeOH leaf extracts by running on 3 MM PC in BAW. All the flavonoid glycoside bands were eluted, combined, concd and hydrolysed with 2N HCl for 1 hr. The acid hydrolysates were extracted with EtOAc and the concd extracts run against standard markers of luteolin, apigenin and tricin by TLC on microcrystalline cellulose in BAW, 50% HOAc, Forestal and CAW (2:1); luteolin and tricin were clearly separated in CAW and spraying with the NA reagent (diphenylboric acid–ethanolamine complex in MeOH), (luteolin-orange and tricin-yellow) allowed trace amounts to be detected.

Identification of methylated flavonols in Cyperus *species.* Methylated flavonols were initially characterized in *C. dactylotes* from a MeOH leaf extract. They were purified by PC on 3 MM paper in (1) BAW and (2) 15% HOAc giving two flavonoid bands, which were run on TLC cellulose in BAW, Forestal, 50% HOAc and CAW (2:1). In 50% HOAc Band 1 gave three compounds and Band 2 two compounds. The main constituents of Band 1, which was dark-yellow in UV + NH_3, co-chromatographed with quercetin 3-methyl ether in BAW, Forestal, 50% HOAc and CAW (2:1) (R_fs: 95, 63; 53 and 59, respectively). The faster running compounds in Band 1 (R_fs: 95, 95; 83, 93; 67, 80 and 98, 98, respectively) appeared to be quercetin 3, 7-dimethyl ether (dark to yellow in UV + NH_3) and quercetin 3, 7, 3′-trimethyl ether (dark-yellow in UV + NH_3) from R_f and UV colour reactions. Band 2 on TLC on cellulose in 50% HOAc gave two constituents, which after elution co-chromatographed with kaempferol 3-methyl ether and kaempferol 3, 7-dimethyl ether, respectively in BAW, Forestal, 50% HOAc and CAW (2:1). R_fs: 96, 96; 84, 95; 75, 84 and 98, 98,

Table 6. R_f data for flavone glycosides and sulphates found in some *Cyperus* species

Flavonoids	BAW	15% HOAc	H_2O	Phenol	Electrophoretic mobility*
Luteolin					
7-glucoside	42	09	02	59	—
7-glucuronide	38	09	41	23	—
Luteolin 5 methyl ether					
7-glucoside	15	13	31	68	—
Tricin					
7-glucoside	59	11	01	90	—
7-glucuronide	24	11	28	71	—
7-sulphate	08	18	81	17	0.28
7-glucosidesulphate	—	—	—	—	0.54
7-glucosidedisulphate?	—	—	—	—	0.95
7-glucuronidesulphate	05	18	81	17	0.75
7-glucuronidedisulphate	05	27	81	—	1.4
Quercetin					
3-glucuronide	49	32	80	12	—

*Electrophoretic mobility in comparison with quercetin 3-sulphate as 1.00.

respectively. Other *Cyperus* species were surveyed for methylated flavonols using the same purification procedures as above before TLC on cellulose in 50% HOAc and Forestal and on Si gel in 10% MeOH–$CHCl_3$ against standard markers and spraying with NA reagent. Quercetin 3-methyl ether, and 3, 7-dimethyl ether gave an orange fluorescence with NA whilst kaempferol 3-methyl ether and 3, 7-dimethyl ether and quercetin 3, 7, 3′-trimethyl ether gave a yellow fluorescence.

Identification of tricin 7-glucuronide sulphate (**1**) *and disulphate* (**2**) *from* C. polystachyos. R_f and electrophoretic data are given in Table 6. Both compounds were isolated from an 80% MeOH leaf/stem extract by paper electrophoresis on 3 MM paper at pH 2.2 for 2 hr. Both **1** and **2** gave tricin, glucuronic acid and sulphate on 1 hr acid hydrolysis (2 N HCl). After 5 min acid hydrolysis **1** gave tricin 7-glucuronide (co-TLC cellulose in four solvents) and **2** gave tricin 7-glucuronide and **1**. β-Glucuronidase hydrolysis of both **1** and **2** gave tricin and sulphatase hydrolysis gave tricin 7-glucuronide. UV λ_{max} nm: **1**, MeOH 258′, 264′, 271, 330; + NaOMe 258′, 264′, 271, 416; + H_3BO_3 258′, 264′, 271, 330; **2**, MeOH 271, 340; + NaOAc 263, 350′, 416; + H_3BO_3 270, 345.

Aurones. Aureusidin was recorded as present only if it was directly apparent, after examining 2-D chromatograms of direct alcoholic extracts in UV light, as a bright yellow spot changing to orange with NH_3, R_f 54 in BAW 0.1 in 15% HOAc. In addition, it was also detected in acid-hydrolysed extracts by 1-D chromatography against an authentic specimen in four solvents. Aureusidin was present in some *Cyperus* species as the glucoside, aureusin (R_f 23 in BAW, 6 in 15% HOAc), which was identified by its acid hydrolysis to give aureusidin and glucose and by its spectral properties. The new aurone mariscetin had R_f values 18 in BAW, 20 in 50% HOAc and UV λ_{max} nm: 257, 325, 414 and also occurred in glycosidic form. The new aurone methyl ether (?) from *C. reflexus* inflorescences had R_f 80 in BAW, 55 in CAW, 59 in PhOH and 45 in 50% HOAc (cf. aureusidin 54, 25, 25, 16 and leptosidin 70, 62, 81, 46).

Tricin 7-sulphate. This was synthesized by standard procedures from tricin and sulphamic acid[3]. Small amounts of the 4′-sulphate were formed, but the major product was the 7-sulphate, the two being separated by chromatography in BAW (R_f 0.66 and 0.30 respectively). The 7-sulphate had UV λ_{max}^{MeOH} nm: 250, 271, 358; + NaOAc, no shift; + $AlCl_3$, 279, 308, 364 and 386.

Acknowledgement—We are grateful to Miss S. S. Hooper, Royal Botanic Gardens, Kew for helpful comments on the taxonomic aspects.

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