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FLAVONOID PATTERNS AND THE REVISED CLASSIFICATION OF AUSTRALIAN RESTIONACEAE‡

IN HONOUR OF PROFESSOR G. H. NEIL TOWERS 75TH BIRTHDAY

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Key Word Index—*Lepyrodia*; *Sporadanthus*; *Calorophus*; Restionaceae; flavonoids; gossypetin; hypolaetin; tricin; sulphates; *C*-glycosides; chemosystematics.

Abstract—The culms of 115 species of Restionaceae endemic to Australia have been surveyed for their flavonoids. Complex patterns are present, based on the occurrences of simple and methylated flavones, gossypetin, hypolaetin, *C*-glycosyl and sulphated flavones. Among aglycones detected for the first time in the family are apigenin, luteolin, chrysoeriol, tricin, kaempferol, quercetin 3-methyl ether, isorhamnetin and the 7-methyl ether of hypolaetin. A variety of new glycosides were also characterised. A study of the distribution of these flavonoids showed that hypolaetin (in 23 of 34 genera), luteolin (in 25 genera), flavone *C*-glycosides (in 13 genera) and sulphates (in 15 genera) are the most typical constituents. By contrast, gossypetin (in 7 genera), tricin (in 7 genera) and myricetin (in 2 genera) are relatively rare. Together, the flavonoid data are generally supportive of the new classification of these plants, which has been mainly based on morphological and anatomical features, supported in part by DNA sequence data. Also significant differences in pattern have emerged compared with the flavonoids of South African species, where flavonols are more common and proanthocyanidins are characteristic.

INTRODUCTION

The Restionaceae are a rush-like group of xeromorphic plants, of some 53 genera and 300 species, which grow almost exclusively either in South Africa or in Australasia. The classification within the family has been inadequate and required major revision, partly because of a dearth of exomorphological features since both their leaves and wind pollinated flowers are highly reduced. In spite of the geographical separation, some generic names have been used for plants from both continents [1, 2]. Following a detailed anatomical survey of the family, Cutler [3, 4] found significant discontinuities among the different groups of plants and concluded that all South African species and genera are distinct from those in Australasia. These conclusions have now been accepted by modern taxonomists. Revisions of South African taxa, based on morphology, anatomy and phytochemistry have been published by Linder [5, 6]. The Australian Restionaceae are being completely revised and of 147 species examined, 57 are newly recognised while 19 of the 34 genera are new or have names that have not been used this century [7–9]. Two genera formerly included in the family, *Lyginia* and *Hopkinsia*, are being separated as monogeneric families [7].

That a phytochemical study of the family might be systematically rewarding was indicated by the earlier discovery of new and rare flavonoid structures in several Australian species. The uncommon yellow flavonol gossypetin was present and the new flavone, 8-hydroxyluteolin (hypolaetin) was reported in *Hypolaena fastigiata* [10]. A more detailed comparison of flavonoid patterns in South African (34 spp.) and Australian plants (14 spp.) showed a number of significant differences. South African plants contained common flavonols, flavones and glycoflavones in most taxa, while the related *Chondropetalum* and *Elegia* additionally yielded glycosides of myricetin, larycitrin and syringetin [6, 11]. By contrast, the small Australian sam-

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‡ In honour of Professor Neil Tower's seventy-fifth birthday.

✠ Deceased 1 August 1997.

ple then available variously contained glycosides of gossypetin, its 7-methyl ether, hypolaetin, myricetin and quercetin and cyanidin 3-glucoside [11].

The opportunity to complete the phytochemical survey of the Australian species arose when authenticated material became available following collecting expeditions of two of us (B.G.B and L.A.S.J.). Here, we report the results of a flavonoid analysis of 115 species of Australian Restionaceae, following their reclassification at the generic and species level [7, 8]. A flavonoid survey of some related plants in Anarthriaceae and Ecdeiocoleaceae has recently been published [12].

Formal botanical naming of the newly recognised genera is in press [9]. Validation of other new names is in preparation; such names are indicated by quotation marks.

RESULTS AND DISCUSSION

The results of a culm (or stem) flavonoid survey of 115 species of Australian Restionaceae are presented in Table 1 arranged according to the latest taxonomic treatment [7]. The profile of this group is very complex with most classes of flavonoid represented, i.e. both simple and methylated flavones and flavonols, 8-hydroxyflavones (hypolaetin) and flavonols (gossypetin), flavone *C*-glycosides, flavonoid sulphates and free aglycones. Flavonoid aglycones recognised in these plants for the first time include the flavones apigenin, luteolin, chrysoeriol and tricin and the flavonols kaempferol, quercetin 3-methyl ether and isorhamnetin. In addition, two new derivatives of hypolaetin (8-hydroxyluteolin) were recognised. One has been provisionally identified as hypolaetin 7-methyl ether (see Experimental). The other is possibly the 7,3′-dimethyl ether, but insufficient material was available to confirm this structural assignment.

The results will be considered at both generic and species levels and for ease of discussion the data for each genus have been summarised in Table 2. These data refer to flavonoid aglycones detected both before and after acid hydrolysis and which are present in the free state possibly on the surface of the culm tissue. The results of a more detailed analysis of the flavonoid glycosides in selected species are presented in Table 3.

The Lepyrodia *Group*

In the new taxonomic treatment of Briggs and Johnson [7] *Lepyrodia*, *Sporadanthus* and *Calorophus* form a group characterised by substomatal cavities, which are often surrounded by protective cells. DNA data give support to this as a basal group within the Australian Restionaceae (Briggs, Marchant, Gilmore and Johnson, unpublished results). Chemically the most clearly defined genus is *Sporadanthus*. The six species of this genus to be transferred from *Lepyrodia*, all have very similar flavonoid patterns in which quercetin and myricetin are almost universal and isorhamnetin is a frequent constituent. Unfortunately we were unable to analyse *S. traversii*, a New Zealand endemic, which was previously the only species placed in the genus, for comparison. Elsewhere in the group infraspecific variation is common, especially in *Lepyrodia* section *Lepyrodia*. Here three chemical groups can be seen (1) flavonols only with patterns similar to those of *Sporadanthus* species: *L.* "*verrucolosa*", *L. scariosa*, *L. muelleri*, *L. monoica* and *L. riparia*; (2) *L. macra* with flavonols and flavonoid sulphates and (3) *L. anarthria*, "*L. cryptica*", *L. leptocaulis* and *L. extensa*, which have flavonols and flavone *C*-glycosides, a pattern also seen in the other two monotypic sections "*Haplophalanae*" and "*Benedictula*". The finding for *L.* "*cryptica*" is of interest. The species closely resembles *L. scariosa* and *L.* "*verruculosa*" in general appearance but the similarity to *L. anarthria* in seed ornamentation suggests a closer relationship to the latter as supported by the flavonoid data. The presence of flavone *C*-glycosides was confirmed in a detailed analysis of *L. anarthria*, where orientin, iso-orientin and a luteolin di-*C*-glycoside were identified together with quercetin 3-glucuronide and an acylated myricetin glycoside.

Flavonol glucuronides were otherwise found only in the related genus *Calorophus*, which consists of two Tasmanian species (one of which also occurs in a very limited part of southern Victoria). *Calorophus elongatus* is otherwise distinct from *Lepyrodia*, *Sporadanthus* and all other Australian Restiads in having a flavonoid profile based on flavonol methyl ethers, present both free and as the 5-glycosides. Quercetin 3-methyl ether was found free, as the 5-glucoside (previously found only in fronds of the fern, *Asplenium trichomanes-ramosum* [13]) and as the new 5-glycoside-3′-sulphate. The second species, *C. erostis* had a much simpler pattern with only one major flavonoid quercetin 3-glucuronide.

The Winifredia *Group*

This is represented by a single species from S.W. Tasmania, *W. sola*. The present chemical data support the isolated position of *Winifredia* as the sole member of its lineage within the Australian Restionaceae in that it has a unique flavonoid profile based simply on flavone *C*-glycosides. However, DNA data (Briggs *et al.*, unpublished results) does not add support for such an isolated position.

The Desmocladus *Group*

This contains seven genera: *Empodisma*, *Coleocarya*, *Desmocladus*, *Harperia*, *Onychosephalum*, *Catacolea*, *Kulinia* and *Lepidobolus*. It is taxonomically a well marked group with a distribution mainly in Western Australia and with several common flora, fruit and anatomical characters.

All the genera are chemically distinct. Thus, *Empodisma* (2 species) with the exception of one accession

of *E. minus* (B. G. Briggs 8251) is characterised by the presence of gossypetin (8-hydroxyquercetin) and luteolin glycosides. However, the two species differ in the additional presence of chrysoeriol, hypolaetin, quercetin and kaempferol in *E. gracillimum* and not in *E. minus*. This is not surprising as they are geographically widely separated, the former in the southwest of Western Australia and the latter in Eastern Australia and New Zealand. Both were once included in *Calorophus* or *Hypolaena* until 1974, when Johnson and Cutler [14] recognised their distinctive features of culm anatomy. Chemically, the presence of quercetin 3-methyl ether, myricetin di- and tri-methyl ether 5-glycosides in *E. minus* (B. G. Briggs 8251) distinguish this plant from the other four accessions sampled and show similarity to *C. elongatus* (accession M. Martin 10.1.66). However, it is distinguished from both taxa in the presence of flavone *C*-glycosides. Otherwise the chemical data are in accord with the separation of *Empodisma* except for the presence of hypolaetin in both *E. gracillimum* and most *Hypolaena* species.

Both accessions of the monotypic genus *Coleocarya*, from high rainfall coastal regions of southern Queensland and northern New South Wales, gave very weak phenolic profiles in which gossypetin was tentatively identified as the only flavonoid component after acid hydrolysis. This would suggest a close relationship with *Empodisma*, which also includes an eastern species of wet or high-rainfall habitats.

Gossypetin is also a characteristic constituent of the single undescribed rare species of *Catacolea*, *C. enodis*, but this taxon is distinguished by the additional presence of the unusual gossypetin 7-methyl ether, quercetin, kaempferol and isorhamnetin. It also differs from all other members of the *Desmocladus* group except *Coleocarya* in lacking flavones.

Flavone *C*-glycosides were found in four of the seven genera in this group: *Desmocladus*, *Harperia*, *Onychosepalum* and *Kulinia*. Both *Desmocladus* and *Harperia* are chemically heterogeneous and are not clearly distinguished from each other. "*Harperia confertospicata*", among the diverse range of Australian taxa formerly placed in *Restio*, differs from both the other two *Harperia* species in producing flavone *C*-glycosides and in the absence of hypolaetin but agrees in the presence of luteolin and tricin, both frequent constituents of the whole group. It is interesting that "*Baloskion fimbriatum*" is the only other species in the present survey with the same aglycone pattern as "*H. confertospicata*". "*Desmocladus quiricanus*", "*D. myriocladus*" and "*D. lateriticus*" were all once included in one variable "species". The present results support their separation in the occurrence of flavone *C*-glycosides only in "*D. myriocladus*", flavonoid sulphates only in "*D. lateriticus*" and tricin, chrysoeriol, quercetin, isorhamnetin and free luteolin and tricin in "*D. quiricanus*".

In the other two flavone *C*-glycoside producing genera, *Onychosepalum* and *Kulinia*, flavones were the only other flavonoid constituents. Taxonomically, *Onychosepalum* is thought to be allied but distinct from *Lepidobolus*. This is reflected in their chemistry. Both produce flavones and lack flavonols but they differ in the presence of apigenin, chrysoeriol and glycoflavones in the former, which are replaced by tricin and free luteolin in the latter.

Kulinia, a rare monotypic genus, has a unique flavonoid pattern amongst Australian Restiads based on chrysoeriol and flavone *C*-glycosides.

The Loxocarya *Group*

The 15 genera include most of the Australian species originally named under *Restio*. The name *Loxocarya* was applied previously to a discordant assemblage of *L. cinerea*, all known *Desmocladus* species and *Hypolaena pubescens*. Only one species of *Loxocarya*, *L. striata*, was included in *Restio* (*R. megalotheca*, a nomenclaturally incorrect name). The remaining genera in the group consist entirely of ex *Restio* or newly distinguished species. Chemically the group has proved to be very diverse with frequent infraspecific variation. No genera, apart from the monotypic *Taraxis* are clearly defined. *Chordifex* was found to be especially heterogeneous with seven different aglycone patterns (Table 4). Hypolaetin, flavone *C*-glycosides, tricin and gossypetin are probably the most useful chemical characters, which might suggest a link between species with patterns 1, 2 and 3 and between patterns 4 and 5.

Of the seven genera thought to be related to *Chordifex* only two monotypic genera, *Dielsia* and *Cytogonidium* and one *Loxocarya* species, *L. cinerea* have the same aglycone pattern (hypolaetin only) as one of the *Chordifex* groups. The others: *Eurychorda*, *Platychorda*, *Tremulina*, *Melanostachya* and the remaining *Loxocarya* species all have patterns distinct from each other and *Chordifex*. *Loxocarya* is especially variable with different profiles for each of the three species surveyed. *Eurychorda complanata* is distinguished by the unusual co-occurrence of the 3- and 7-glycosides of gossypetin (Table 3). Gossypetin was otherwise detected in only one *Chordifex* species, *C. abortivus* in the *Loxocarya* group.

Baloskion is another chemically heterogeneous genus with many chemovars. Species profiles include luteolin, tricin, quercetin, gossypetin and glycoflavones. This genus has distinctive flower position and seed structure but has fruit and anatomical features in common with the new monotypic genera *Guringalia* and *Saropsis*, but chemically these differ in the presence of hypolaetin and flavonoid sulphates and the absence of gossypetin in all except one accession of *S. fastigiatum*. Another new genus *Acion* is not chemically clearly distinguished from *Baloskion* in the co-occurrence of luteolin, tricin and hypolaetin, a pattern seen also in "*B. australe*" and "*B. longipes*".

The genus *Alexgeorgea* is morphologically so distinct as to be described as bizarre by Carlquist [15], with female flowers arising below ground level so that

Table 1. The distribution of culm flavonoids in Australian Restionaceae*

	Flavones					Flavonols					Other	Flavone	Flavonoid	Glucuronides	Collector's
	Lu	Ap	Tr	Chrys	Hyp	My	Qu	Km	Isorh	Goss	Aglycones	C-glyc	sulphates	present	name & number
Lepyrodia R.Br.															
Section *Leprodia*															
L. anarthria F. Muell.	–	–	–	–	–	+	+	–	–	–	–	+	–	–	S. Krauss 98
L. "cryptica" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	–	–	–	–	–	+	–	–	L. A. S. Johnson 8025b
L. "verruculosa" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	+	–	+	–	–	–	–	–	B. G. Briggs 9267
L. scariosa R.Br	–	–	–	–	–	–	+	–	+	–	–	–	–	–	S. Krauss 125
	–	–	–	–	–	–	+	–	+	–	–	–	–	–	S. Krauss 128
L. leptocaulis L. A. S. Johnson and O. D. Evans	–	–	–	–	–	+	+	–	–	–	–	+	–	–	S. Krauss 104
	–	–	–	–	–	+	+	–	–	–	–	+	–	–	S. Krauss 105
L. muelleri Benth	–	–	–	–	–	+	+	–	–	–	–	–	–	–	S. Krauss 43
L. "extensa" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	+	+	–	–	–	(+)	–	–	B. G. Briggs 7594
	–	–	–	–	–	–	+	+	–	–	–	(+)	–	–	B. G. Briggs 7616
L. macra Nees	–	–	–	–	–	–	+	–	–	+	–	–	+	–	R. Coveny 8136
	–	–	–	–	–	–	+	–	–	+	–	–	+	–	D. J. McGillivray 3470
L. hermaphrodita R.Br	–	–	–	–	–	–	+	–	+	–	–	–	–	–	B. G. Briggs 7647
	–	–	–	–	–	–	+	–	+	–	–	–	+	–	B. G. Briggs 7612
L. monoica F. Muell.	–	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 8465
L. "riparia" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 8285
Section "Haplophalanx" L. A. S. Johnson and B. G. Briggs unpubl.															
L. glauca (Nees) F. Muell.	–	–	–	–	–	–	+	–	–	–	–	+	–	–	B. G. Briggs 7532
	–	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 8291
Section "Benedictula" L. A. S. Johnson and B. G. Briggs unpubl.															
L. heleocharoides Gilg	–	–	–	–	–	–	+	–	+	–	–	+	–	–	B. G. Briggs 8355
Sporadanthus F. Muell.															
S. gracilis (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	+	–	+	–	–	–	–	–	R. Coveny 11205

S. tasmanicus (Hook. f.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	(+)	+	–	–	–	–	–	–	B. G. Briggs 7111
	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 8246
	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 8250
S. interruptus (F. Muell.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	+	–	–	–	–	–	–	S. Krauss 50
	–	–	–	–	–	+	+	–	–	–	–	–	–	S. Krauss 13
S. caudatus (L. A. S. Johnson and O. D. Evans) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	+	–	–	–	Fl green cpd	–	–	S. Krauss 68
S. strictus (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	+	–	–	–	–	–	–	B. G. Briggs 7587 and L. A. S. Johnson
S. rivularis L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	+	+	–	+	–	–	–	–	B. G. Briggs 8287
Calorphus Labill.														
C. elongatus Labill.	–	–	–	–	–	–	+	–	–	–	Qu3Me free and in glycosidic comb.	–	+	+	M. Martin 10.1.66
C. erostis (C. B. Clarke) L. A. S. Johnson and B. G. Briggs	–	–	–	–	–	–	+	–	–	–	–	–	–	+	J. Jarman 9.3.85
Winifredia L. A. S. Johnson and B. G. Briggs														
W. sola L. A. S. Johnson and B. G. Briggs	–	–	–	–	–	–	–	–	–	–	–	+	–	–	K. L. Wilson 8470
	–	–	–	–	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 9109
Empodisma L. A. S. Johnson and D. Cutler														
E. gracillimum (F. Muell.) L. A. S. Johnson and D. F. Cutler	+	–	–	–	+	–	–	–	–	+	–	–	–	–	B. G. Briggs 7607
	+	–	–	+	+	–	–	–	–	+?	–	–	–	–	B. G. Briggs 7620
E. minus (Hook. f.) L. A. S. Johnson and D. F. Cutler	–	–	–	–	–	–	–	–	–	–	Qu 3ME, My DIME and triME in glycosidic comb.	–	–	–	B. G. Briggs 8251
	+	–	–	–	–	–	+	+	–	+	–	–	–	–	B. G. Briggs 8018
	–	–	–	–	–	–	+	+	–	+	–	–	–	–	S. Krauss 73
	+	–	–	–	–	–	+	+	–	+	–	–	–	–	B. G. Briggs 8238
	+	–	–	–	–	–	+	–	–	+	–	–	–	–	B. G. Briggs 8237

Table 1.—*Continued.*

	Flavones					Flavonols									
	Lu	Ap	Tr	Chrys	Hyp	My	Qu	Km	Isorh	Goss	Other Aglycones	Flavone C-glyc	Flavonoid sulphates	Glucuronides present	Collector's name & number
Coleocarya S. T. Blake															
C. gracilis S. T. Blake	–	–	–	–	–	–	–	–	–	+?	–	–	–	–	S. Krauss 60
	–	–	–	–	–	–	–	–	–	+?	–	–	–	–	S. Krauss 70
Desmocladus Nees															
D. myriocladus (Gilg) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 8550
D. "quiricanus" L. A. S. Johnson and B. G. Briggs unpubl.	(+)	–	+	–	–	–	+	–	(+)	–	Free Lu, and Tricin	–	–	–	B. G. Briggs 7913
	+	–	+	–	–	–	+	–	–	–	Free Lu, and Tricin	–	–	–	B. G. Briggs 7917
D. "lateriticus" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+?	–	–	–	–	–	–	–	+	–	B. Briggs 7437
D. "austrinus" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 6632
D. virgatus (Benth.) L. A. S. Johnson and B. G. Briggs	+	–	–	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 7459
D. flexuosus L. A. S. Johnson and B. G. Briggs unpubl.	(+)	–	–	+	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 6553
D. asper (Nees) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 6798
	+	–	+	–	+	–	–	–	–	–	–	–	–	–	T. & J. Whaite 4100
D. "tenuis" L. A. S. Johnson and B. G. Briggs unpubl.	No flavonoids detected														B. G. Briggs 7670
	No flavonoids detected														B. G. Briggs 7885
D. fasciulatus (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	(+)	–	–	–	–	–	–	–	Free Lu	+	–	–	B. G. Briggs 7664
	–	–	+	–	–	–	–	–	–	–	Free Lu	+	–	–	B. G. Briggs 7641
D. "castaneus" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 7659
	–	–	–	–	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 7660
D. "elongatus" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	(+)	–	–	–	–	–	–	–	Free Lu, and Tricin 2Dk/Dk free unknowns	+	–	–	B. G. Briggs 7481
	–	–	–	–	–	–	–	–	–	–	Free Lu	+	–	–	B. G. Briggs 7483

D. "semiplanus" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	–	–	–	–	Free Lu Aca? unknown Dk/Y after acid hyd	–	–	–	L. Haegi 1922
	Aglycones too weak										Same as above?	–	–	–	B. G. Briggs 7498
D. "parthenicus" L. A. S. Johnson and B. G. Briggs unpubl.	(+)?	–	(+)	–	(+)?	–	–	–	–	–	Free Lu and Tricin	–	–	–	B. G. Briggs 7458
	(+)?	–	(+)	–	(+)?	–	–	–	–	–	Free Lu and Tricin	–	–	–	B. G. Briggs 7486
Harperia W. Fitz															
H. lateriflora W. Fitzg.	+	–	+	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7507
H. confertospicatus (Steud.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 7665
H. "eyreana" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	(+)	–	+	–	–	–	–	–	Free Lu, and Tricin	–	–	–	Jacobs 7052
Onychosepalum Steud															
O. laxiflorum Steud	+	+	–	–	–	–	–	–	–	–	–	+	+	–	B. G. Briggs 7888
	+	+	–	–	–	–	–	–	–	–	–	+	+	–	B. G. Briggs 7656
	+	+	–	–	–	–	–	–	–	–	–	+	+	–	B. G. Briggs 7661
O. microcarpum L. A. Meney and J. S. Pate	+	–	–	+	–	–	–	–	–	–	–	–	–	–	J. Pate NSW 284675
Catacolea B. G. Briggs and L. A. S. Johnson in press															
Catacolea enodis B. G. Briggs and L. A. S. Johnson in press	–	–	–	–	–	–	+	(+)	(+)	+	Goss 7Me	–	+	–	B. G. Briggs 7728
	–	–	–	–	–	–	+	+	(+)	+	Goss 7Me	–	+	–	B. G. Briggs 7729
	–	–	–	–	–	–	+	(+)	(+)	+	Goss 7Me	–	–	–	B. G. Briggs 7740
	–	–	–	–	–	–	+	(+)	(+)	+	Goss 7Me	–	(+)	–	B. G. Briggs 7739
Kulinia B. G. Briggs and L. A. S. Johnson in press															
Kulinia eludens B. G. Briggs and L. A. S. Johnson in press	–	–	–	–	–	–	–	–	–	–	B/Y unknown	–	–	–	B. G. Briggs 8530
	–	–	–	(+)	–	–	–	–	–	–	–	+	–	–	B. G. Briggs 8531
Lepidobolus Nees															
L. preissianus Nees ssp. *preissianus*	+	–	–	+	–	–	–	–	–	–	Unknown Dk/Dk	–	–	–	K. L. Wilson 2674

Table 1.—*Continued*

	Flavones					Flavonols					Other	Flavone	Flavonoid	Glucuronides	Collector's
	Lu	Ap	Tr	Chrys	Hyp	My	Qu	Km	Isorh	Goss	Aglycones	C-glyc	sulphates	present	name & number
L. "densus" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	–	–	–	–	–	–	Free Lu + unknown Dk/Dk	–	–	–	B. G. Briggs 7755
	+	–	+	–	–	–	–	–	–	–	–	–	–	–	B. G. Briggs 7757
L. deserti Gilg															
L. chaetocephalus F. Muell. ex Benth.	+	–	+	–	–	–	–	–	–	–	2 DK/Dk unknowns	–	–	–	B. G. Briggs 7511
	+	–	+	–	–	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 7512
L. "quadratus" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	–	–	+	–	–	–	2 Dk/Dk unknowns	–	–	–	K. L. Wilson 2706
	+	–	+	–	–	–	+	–	–	–	Dk/Dk unknowns	–	–	–	B. G. Briggs 7457
Baloskion Raf.															
B. gracile (R.Br) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	–	–	+	–	–	+	–	–	–	–	S. Krauss 129
B. australe (R.Br) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	+	–	–	–	–	–	Free Tricin, and Lu	–	–	–	S. Krauss 116
B. longipes (L. A. S. Johnson and O. D. Evans) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	+	–	–	–	–	–	Anthocyanin	–	–	–	S. Krauss 115
B. stenocoleum (L. A. S. Johnson and O. D. Evans) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	–	–	–	–	–	+	–	–	–	–	S. Krauss 93
B. fimbriatum L. A. S. Johnson and O. D. Evans) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	–	–	–	–	–	–	–	+	–	–	S. Krauss 112
B. pallens (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	(+)	–	–	–	–	–	(+)	–	–	+	Anthocyanin (Cy glyc)	–	–	–	S. Krauss 36
	+	–	–	–		–	+	–	–	+	–	–	–	–	S. Krauss 37
B. tenuiculme (S. T. Blake) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	–	–	+	–	–	+	Anthocyanin	–	–	–	S. Krauss 64
	(+)	–	(+)	–	–	–	+	–	–	–	Anthocyanin	–	–	–	S. Krauss 56
B. tetraphyllum (Labill.) L. A. S. Johnson and B. G. Briggs unpubl. ssp *tetraphyllum*	No flavonoids detected														B. G. Briggs 7103
	+	–	+	Tri	+	–	+	–	–	–	–	–	–	–	B. G. Briggs 8247

B. tetraphyllum ssp. *meiostachum* (L. A. S. Johnson and O. D. Evans) L. A. S. Johnson and B. G. Briggs unpubl.	No flavonoids detected, many blue compounds														S. Krauss 69
Guringalia															
G. dimorpha (R.Br.) B. G. Briggs and L. A. S. Johnson in press	+	–	–	–	+	–	–	–	–	–	–	–	+	–	S. Krauss 127
	+	–	–	–	+	–	–	–	–	–	–	–	+	–	S. Krauss 127
Acion B. G. Briggs and L. A. S. Johnson in press															
A. hookeri (D. J. Morris) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	+	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 8249
	+	–	+	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 8245
	+	–	+	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 8254
Saropsis B. G. Briggs and L. A. S. Johnson in press															
S. fastigiatum (R.Br.) B. G. Briggs and L. A. S. Johnson in press	+	–	–	–	+	–	+	–	–	–	–	–	–	–	S. Krauss 124
	–	–	–	–	+	–	–	–	–	–	–	–	–	–	S. Krauss 85
	+	–	–	+	+	–	–	–	–	+	–	–	+	–	Johnson 47814
Alexgeorgea Carlquist															
A. nitens (Nees) L. A. S. Johnson and B. G. Briggs	+	–	+	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 6311
	No visible flavonoids														B. G. Briggs 6292
	No visible flavonoids														R. Coveny 8200
	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 6758
A. subterranea Carlquist	+	–	+	–	+	–	–	–	–	–	Free (Aca)? and Tricin	–	–	–	B. G. Briggs 7463
	+	–	+	–	–	–	–	–	–	–	Free Lu, Aca? and Tricin	–	–	–	B. G. Briggs 7724
A. ganopoda L. A. S. Johnson and B. G. Briggs	+	–	+	–	+	–	–	–	–	–	Free Lu and tricin	–	–	–	B. G. Briggs 6939
Chordifex B. G. Briggs and L. A. S. Johnson in press															
C. laxus (R.Br.) L. A. S. Johnson and B. G. Briggs in press	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7715
	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7558
C. gracillior (F. Muell. ex Benth) L. A. S. Johnson and B. G. Briggs unpubl.	No flavonoids detected														B. G. Briggs 7586
	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7587

Table 1.—*Continued.*

	Flavones Lu	Ap	Tr	Chrys	Hyp	Flavonols My	Qu	Km	Isorh	Goss	Other Aglycones	Flavone C-glyc	Flavonoid sulphates	Glucuronides present	Collector's name & number
C. ornatus (Steud.) L. A. S. Johnson and B. G. Briggs in press	–	–	+	–	–	–	+	–	+	–	Dk/Dk unknown	–	–	–	B. G. Briggs 8498
	–	–	+	–	–	–	+	–	+	–	Dk/Dk unknown	–	–	–	B. G. Briggs 8499
C. "capillaceus" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	–	–	–	–	Anthocyanin	+	–	–	B. G. Briggs 6603
	–	–	–	–	–	–	–	–	–	–	Anthocyanin	+	–	–	B. G. Briggs 6598
C. "microcodon" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	+	–	–	–	+	+	–	+	–	–	–	–	B. G. Briggs 7490
	–	–	+	–	–	–	+	+	–	+	–	–	–	–	B. G. Briggs 7447
C. "sinuosus" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	+	–	L. Haegi 1927
C. "chaunocoleus" (F. Muell.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 8636
C. "serialis" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	+	–	–	–	–	–	Dk/Dk free unknown	–	+	–	B. G. Briggs 6652
	–	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 6645
C. stenandrus B. G. Briggs and L. A. S. Johnson in press	–	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 7473
	–	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 7475
C. abortivus (Nees) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	+	+	–		–	–	+	–	–	+	–	B. G. Briggs 8702
C. leucoblepharus (Gilg) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	+	–	–	–	–	–	–	Free Chrys Dk/Dk unknown	–	–	–	B. G. Briggs 7900
C. amblycoleus (F. Muell.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7574
	–	–	–	–	(+)?	Aglycones very weak but dK/Dk glyc present									B. G. Briggs 7575
C. "jacksonii" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	–	–	–	–	–	–	–	+	+	–	B. G. Briggs 9078
Dielsia Gilg															
D. stenostachya (W. Fitzg.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7799

Eurychorda B. G. Briggs and L. A. S. Johnson in press															
E. complanata (R.Br.) B. G. Briggs and L. A. S. Johnson in press	+	–	+	–	–	–	–	–	–	+	Free Lu	–	–	–	B. G. Briggs 8239
	+	–	+	–	+	–	–	–	–	+	Anthocyanin (Cy glyc)	–	–	–	S. Krauss 51
Platychorda B. G. Briggs and L. A. S. Johnson in press															
P. applanata (Spreng.) B. G. Briggs and L. A. S. Johnson in press	+	+	–	–	–	–	–	–	–	–	Free Lu Dk/Dk unknown	–	–	–	B. G. Briggs 7569
Tremulina B. G. Briggs and L. A. S. Johnson in press															
T. tremula (R.Br.) B. G. Briggs and L. A. S. Johnson in press	+	–	–	+	–	–	–	–	–	–	Free Chrys and Lu Dk/Dk unknown	–	–	–	B. G. Briggs 7635
T. "cracens" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 6931a
Melanostachya B. G. Briggs and L. A. S. Johnson in press															
M. ustulata (F. Muell. ex Ewart and Sharman) B. G. Briggs and L. A. S. Johnson in press	Aglycones too weak										Pro Cy Dk/Dk, 1 Dk/Y glycs	–	–	–	B. G. Briggs 7564
	(+)	–	–	–	+	–	(+)	–	–	–		+	–	–	J. W. Wrigley 4713
Cytogonidium B. G. Briggs and L. A. S. Johnson in press															
C. leptocarpoides (Benth.) B. G. Briggs and L. A. S. Johnson in press	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7552
Loxocarya R.Br.															
L. striata (F. Muell.) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	+	–	+	–	–	–	–	–	K. L. Wilson 2819
	–	–	–	–	+	–	–	+	–	–	Dk/Dk unknown poss 80H Ap	–	–	–	B. G. Briggs 6661
L. "gigas" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	+	–	–	–	Unknown Dk/Dk after hyd	–	–	–	B. G. Briggs 7727
	–	–	–	–	–	–	+	–	–	–	Unknown Dk/Dk after hyd	–	–	–	B. G. Briggs 7738
L. cinerea R.Br.	–	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 8389
Taraxis B. G. Briggs and L. A. S. Johnson in press															

Table 1.—*Continued*

	Flavones					Flavonols					Other	Flavone	Flavonoid	Glucuronides	Collector's
	Lu	Ap	Tr	Chrys	Hyp	My	Qu	Km	Isorh	Goss	Aglycones	C-glyc	sulphates	present	name & number
T. grossa B. G. Briggs and L. A. S. Johnson in press	+	–	–	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 8366
	+	–	–	–	+	–	–	–	–	–	Free Lu	–	–	–	B. G. Briggs 8327
Tyrbastes B. G. Briggs and L. A. S. Johnson in press															
T. glaucescens B. G. Briggs and L. A. S. Johnson in press	+	–	+	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 8338
	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 8337
Leptocarpus R.Br.															
L. tenax (Labill.) R.Br.	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7Me and DiMe	–	+	–	S. Krauss 35
	–	–	–	–	+	–	–	–	–	–	Hypolaetin 7Me and another Dk/Dk unknown	–	+	–	B. G. Briggs 7039
	–	–	–	–	–	–	–	–	–	–	"	–	–	–	B. G. Briggs 8243
	–	–	–	–	–	–	–	–	–	–	"	–	–	+	B. G. Briggs 8248
	+	–	–	–	–	–	–	–	–	–	Hypolaetin? 8ME + diMe	–	+	+	B. G. Briggs 7567
L. "elegans" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 7553
	+	–	–	+	+	–	–	–	–	–	Dk/Dk unknown	–		–	B. G. Briggs 7555
"*L. diffusus*" (Spreng.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7Me, Dk/Dk unknown	–	+	+	B. G. Briggs 7535
	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7Me Dk/Dk unknown	–	+	+	B. G. Briggs 7577
Hypolaena R.Br.															
Section "*Homeolaena*" L. A. S. Johnson and B. G. Briggs unpubl.															
H. humilis (Gilg) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	–	–	–	–	–	–	Dk/Dk unknown	–	+	–	K. L. Wilson 2807
Section "*Hypolaena*" L. A. S. Johnson and B. G. Briggs unpubl.															

H. exsulca R.Br.	+	–	–	–	+	–	–	–	–	–	–	–	+	–	P. G. Wilson 8106
	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 8415
H. "viridus" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	+	–	–	–	–	–	–	–	(+)?	–	B. G. Briggs 7571
H. fastigiata R. Br.	+	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 7628
	+	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 7640
	+	–	–	–	+	–	–	–	–	–	–	–	+	–	S. Krauss 53
H. pubescens (R.Br.) Nees	+	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 566
	+	–	–	–	+	–	–	–	–	–	–	–	+	–	B. G. Briggs 7541
Stenotalis B. G. Briggs and L. A. S. Johnson in press															
S. ramosissima (Gilg) B. G. Briggs and L. A. S. Johnson in press	+	–	–	–	+	–	+	–	–	–	–	–	+	+	B. G. Briggs 6494
	+?	–	–	–	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 6461
Meeboldina Suess.															
M. "roycei" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME?	–	+	+	P. G. Wilson 6258
M. "thysanantha" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	+	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 7630
M. "crebriculmis" L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	Anthocyanin hypolaetin 7ME?	–	+	+	B. G. Briggs 7547
	+	–	–	–	+	–	–	–	–	–	Anthocyanin hypolaetin 7ME?	–	+	+	B. G. Briggs 7549
"M. scariosa" (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME?	–	+	+	B. G. Briggs 7570
M. "tephrina" L. A. S. Johnson and B. G. Briggs unpubl.	–?	–	–	–	+	–	–	–	–	–	Anthocyanin	–	+	+	B. G. Briggs 7583
	+	–	–	–	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 7537
M. cana (Nees) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 8296
M. "kraussii" L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME? 80H Ap?	–	+	+	B. G. Briggs 7652
	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME?	–	+	?	B. G. Briggs 7667
Chaetanthus R.Br.															
C. aristatus (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME 80H Ap?	–	+	+	B. G. Briggs 7559
	–	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME?	–	+	+	K. L. Wilson 2744
	–	–	–	–	+	–	–	–	–	–	Hypolaetin 7ME?	–	+	+	K. L. Wilson 2743

Table 1.—*Continued*

	Flavones					Flavonols					Other	Flavone	Flavonoid	Glucuronides	Collector's
	Lu	Ap	Tr	Chrys	Hyp	My	Qu	Km	Isorh	Goss	Aglycones	C-glyc	sulphates	present	name & number
C. tennellus (Nees) F. Muell.	+	–	–	–	+	–	–	–	–	–	–	–	–	–	B. G. Briggs 7663
C. leptocarpoides R.Br.	+	–	–	–	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 7582
	+	–	–	–	+	–	–	–	–	–	–	–	+	+	B. G. Briggs 7582a
Apodasmia B. G. Briggs and L. A. S. Johnson in press															
A. chilensis (Gay) L. A. S. Johnson and B. G. Briggs unpubl.	–	–	–	–	–	–	–	–	–	–	Goss 7ME	–	–	–	ex Concepcion
A. brownii (Hook. f.) B. G. Briggs and L. A. S. Johnson in press	–	–	–	–	–	–	–	–	–	–	Goss 7ME	–	–	–	B. G. Briggs 5421
	–	–	–	–	–	–	–	–	–	–	Goss 7ME and another Dk/Dk aglycone	–	–	–	B. G. Briggs 2922
A. "ceramophila" B. G. Briggs and L. A. S. Johnson unpubl.	–	–	–	–	+	–	–	–	–	+	Goss 7ME	–	–	–	B. G. Briggs 8292
	+	–	–	–	+	–	+	–	+	–	Goss 7Me	–	–	–	B. G. Briggs 8293
Dapsilanthus B. G. Briggs and L. A. S. Johnson in press															
D. spathaceus (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–		–	–	+	B. G. Briggs 7310
D. elatior (R.Br.) B. G. Briggs and L. A. S. Johnson in press	Very weak														B. G. Briggs 7300
D. ramosus (R.Br.) L. A. S. Johnson and B. G. Briggs unpubl.	+	–	–	–	+	–	–	–	–	–	–	–	–	–	S. W. L. Jacobs 6298

Key: Lu = luteolin, Ap = apigenin, Hyp = hypolaetin, My = myricetin, Qu = quercetin, Km = kaempferol, Isorh = isorhamnetin, Goss = gossypetin, Az = azaleatin, ProCy = procyanidin, Dk/Y = dark to yellow in UV light + NH_3.

* Classification according to B. G. Briggs and L. A. S. Johnson [7–9].

Table 2. The % occurrence of culm flavonoids in Australian genera of the Restionaceae*

Genus	No of spp. analysed	Flavones†						Flavonols†							Free Aglycones						Characteristic constituents
		Lu	Ap	Tr	Chrys	Hyp	Hyp 7ME	My	Qu	Km	Isorh	Goss	Goss 7ME	Qu 3ME	Lu	Tr	Chrys	Qu 3ME	Flavone *C*-glycs	Flavonoid sulphates	
Lepyrodia Section	11	0	0	0	0	0	0	45	90	27	27	0	0	0	0	0	0	0	8	18	My, Qu, Km, Isorh, *C*-glys, SO_4s
Lepyrodia Section	1	0	0	0	0	0	0	0	100	50	0	0	0	0	0	0	0	0	100	0	Qu, Km, *C*-glycs
Haplophalanae Section	1	0	0	0	0	0	0	0	100	0	9	0	0	0	0	0	0	0	100	0	Qu, *C*-glycs
Benedictula																					
Sporadanthus	6	0	0	0	0	0	0	83	100	0	33	0	0	0	0	0	0	0	0	0	My, Qu, Isorh
*Calorophus***	2	0	0	0	0	0	0	0	50	0	0	0	0	100	0	0	0	50	0	50	Qu3ME, MydiMe other flavonol MEs
Winifredia	1	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0	*C*-glycs
Empodisma	2	100	0	0	50	50	0	0	50	50	0	100	0	0	0	0	0	0	0	0	Goss, Lu, Chrys, Hyp, Qu, Km
Coleocarya	1	0	0	0	0	0	0	0	0	0	0	100?	0	0	0	0	0	0	0	0	Goss
Desmocladus	13	54	0	46	8	39	0	0	8	0	8	0	0	0	46	23	0	0	31	15	Lu, Tr, Hyp, Qu, Isorh, Free Lu and Tricin, C-glycs, SO_4s
Harperia	3	100	0	100	0	67	0	0	0	0	0	0	0	0	33	33	0	0	33	0	Lu, Tr, Hyp, Free Lu Tr, *C*-glys
Onychosepalum	2	100	50	0	50	0	0	0	0	0	0	0	0	0	0	0	0	0	100	100	Lu, Ap, Chrys *C*-glycs, SO_4s
Catacolea	1	0	0	0	0	0	0	0	100	100	100	100	100	0	0	0	0	0	0	100	Goss, Goss 7ME, Qu, Km, Isorh, SO_4s
Kulinia	1	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	100	0	Chrys, *C*-glycs
Lepidobolus	5	100	0	80	0	0	0	0	0	0	0	0	0	0	20	0	0	0	0	0	Lu, Tr, Free Lu
Baloskion	9	100	0	56	0	33	0	0	44	0	0	44	0	0	11	11	0	0	11	0	Goss, Lu, Tr, Hyp, Qu, Free Lu and Tr, *C*-glycs
Guringalia	1	100	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	100	Lu, Hyp, SO_4s
Acion	2	50	0	50	0	100	0	0	0	0	0	0	0	0	100	0	0	0	0	50	Lu, Tr, Chrys, Hyp, Qu, Goss, SO_4s
Saropsis	1	100	0	0	100	100	0	0	100	0	0	100	0	0	0	0	0	0	0	100	Lu, Hyp
Alexgeorgea	3	100	0	100	0	100	0	0	0	0	0	0	0	0	67	67	0	0	0	0	Lu, Tr, Hyp

Table 2.—*Continued*

Genus	No of spp. analysed	Flavones†						Flavonols†							Free Aglycones						Characteristic constituents
		Lu	Ap	Tr	Chrys	Hyp	Hyp 7ME	My	Qu	Km	Isorh	Goss	Goss 7ME	Qu 3ME	Lu	Tr	Chrys	Qu 3ME	Flavone *C*-glycs	Flavonoid sulphates	
Chordiflex	14	31	0	15	15	61	0	0	23	8	8	15	0	0	0	8	0	0	15	46	Lu, Tr, Chrys, Hyp, QuGoss, *C*-glys, SO_4s
Dielsia	1	0	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	Hyp
Eurychorda	1	100	0	100	0	100	0	0	0	0	0	100	0	0	100	0	0	0	0	0	Lu, Tr, Hyp, Goss, Free Lu
Platychorda	1	100	100	0	0	0	0	0	0	0	0	0	0	0	100	0	0	0	0	0	Lu, Free Lu
Tremulina	2	100	0	0	50	50	0	0	0	0	0	0	0	0	50	0	50	0	0	0	Lu, Hyp, Chrys free Lu
Melanostachya	1	(100)	0	0	0	100	0	0	(100)	0	0	0	0	0	0	0	0	0	100	0	Hyp, *C*-glycs
Cytogonidium	1	0	0	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	Hyp
Loxocarya	3	0	0	0	0	67	0	0	67	33	33	0	0	0	0	0	0	0	0	0	Hyp, Qu, Km, Isorh
Taraxis	100	0	0	0	100	0	0	0	0	0	0	0	0	0	100	0	0	0	0	0	Lu, Hyp free, Lu
Tyrbastes	100	0	100	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	Lu, Tr, Hyp
Leptocarpus	3	100	0	0	33	100	67	0	0	0	0	0	0	0	0	0	0	0	0	0	Lu, Hyp, Hyp7-ME and DIME, Chrys
Hypolaena section "*Homeolaena*"	1	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	Lu, SO_4s
Section "*Hypolaena*"	4	100	0	0	100	0	0	0	0	0	0	0	0	0	0	0	0	0	0	100	Lu, Hyp, SO_4s
Stenotalis	1	100	0	0	0	100	0	0	100	0	0	0	0	0	0	0	0	0	0	100	Lu, Hyp, Qu, SO_4s
Meeboldina	7	100	0	0	0	100	57	0	0	0	0	0	0	0	0	0	0	0	0	86	Lu, Hyp, Hyp-7ME, SO_4s
Chaetanthus	3	100	0	0	0	100	33	0	0	0	0	0	0	0	0	0	0	0	0	67	Lu, Hyp, Hyp7-ME, SO_4s
Apodasmia	3	33	0	0	0	33	0	0	33	0	33	33	100	0	0	0	0	0	0	0	Lu, Hyp, Qu, Isorh, Goss, Goss7ME
Dapsilanthus	3	100	0	0	0	67	33?	0	0	0	0	0	0	0	0	0	0	0	33?	33	Lu, Hyp, *C*-glycs?SO_4

* Classification according to B. G. Briggs and L. A. S. Johnson [7–9].
† Detected after acid hydrolysis.
** A myricetin dimethyl ether also present in one species.
( ) Present in trace amount.
In the rare cases where different accessions of a species vary, the accession with the most constituents has been regarded as characteristic of that species.

Table 3. Flavonoid glycosides identified in some Restionaceae species

Species	Flavonoid glycosides
Apodasmia brownii B. G. Briggs 2922	Goss 7ME 3-Glc-8-Gal or 3-Gal-8-Glc
A. chilensis ex Concepcion, Chile	
Calorophus elongatus M. Martin 10.1.66	Qu 3ME 5-glyc, My di- and tri-ME 5-glycs, flavone *C*-glycs
C. erostis J. Jarman 9.3.85	Qu 3-Glur
Empodisma minus Accession 1 B. G. Briggs 8237	Goss 7-Glc, Qu and Km 7-glycs, Lu glyc
E. minus Accession 2 B. G. Briggs 8251	Qu 3-Glur, Qu 3ME 5-Glc-3′-SO_4, Qu 3ME 5-Glc, free Qu 3ME
Eurychorda complanata B. G. Briggs 8239	Goss 7-Glc, Goss 3-Glc, Qu 3-Rha, Lu and Tricin diglycosides
Hypolaena fastigiata B. G. Briggs 7640	Hypolaetin 7-SO_4-8-Glc, Lu 7-SO_4
Leptocarpus elegans B. G. Briggs 7555	Hypolaetin 7-glyc SO_4, Hypolaetin 7 ME 3′-Glur SO_4, Hypolaetin 7, 3′-DIME 4′-Glc, Lu and Chrys 7-Glur SO_4
L. tenax B. G. Briggs 7039	Hypolaetin 7ME 3′-Gal SO_4
Lepyrodia anarthria S. Krauss 98	Orientin, Iso-orientin, Lu di-*C*-glyc, Qu 3-Glur, acylated My glyc
"*Meeboldina thysanantha*" B. G. Briggs 7630	Hypolaetin 7-Glur SO_4, Lu and Chrys 7-Glur SO_4, Lu 7-Glc and Gal
Winifredia sola B. G. Briggs 9109	Ap and Lu di-*C*-glycosides

Table 4. Flavonoid aglycone variation amongst *Chordiflex* species

Flavonoid aglycone pattern	*Chordiflex* species
1. Hypolaetin only	*C. laxus*, *C. crispatus*, *C.* "*serialis*" *C. stenandrus* and *C. amblycoleus*
2. Hypolaetin + luteolin	*C. chaunocoleus*
3. Hypolaetin + chrysoeriol and quercetin	*C. abortivus*
4. Flavone *C*-glycosides only	*C. capillaceus*
5. Flavone *C*-glycosides + luteolin	"*C. jacksonii*"
6. Tricin, quercetin and isorhamnetin	*C. ornatus*
7. Tricin, quercetin, kaempferol and gossypetin	"*C. microdon*"

only the long style is visible. The three species also have the largest fruits in the Restionaceae. Despite some infraspecific chemical variation, this genus does have a unique profile (hypolaetin, luteolin and tricin) which adds support to the view that it has not evolved as a specialisation from within *Chordifex* [7], where this pattern is not seen.

The new monotypic genera *Taraxis* and *Tyrbastes* both occur in wet areas of southwestern Australia and have a trailing, repeatedly branching habit and 1-flowered female spikelets. However, they differ in other floral and anatomical characters. Similarly in their chemistry, they both have a basic luteolin/hypolaetin profile but differ in the presence of tricin in the latter and free luteolin in the former.

The Leptocarpus *Group*

The genus *Leptocarpus*, which once contained ten Australian species and one species each from New Zealand, Chile and S.E. Asia is now restricted to three Australian species in the new classification, while *Meeboldina* has been greatly enlarged. *Chaetanthus* and *Hypolaena* have been retained (with some enlargement) and three new genera recognised: *Stenotalis*, *Apodasmia* and *Dapsilanthus*.

The three *Leptocarpus* species all have the same distinctive flavonoid aglycone pattern of luteolin, hypolaetin, hypolaetin 7-methyl ether and a hypolaetin dimethyl ether. However, this pattern also occurs in five of the seven *Meeboldina* species and in one of the three *Chaetanthus* species surveyed, *C. aristatus*. Hypolaetin was detected in all species of this group except for "*Hypolaena humilis*" and some accessions of *L. tenax*, where hypolaetin mono- and dimethyl ethers are the major constituents.

Chemically most members of the *Leptocarpus* group appear to be very closely related but there is also some evidence to support the recognition of the three new genera. Thus, *Apodasmia*, despite the wide and disjunct distribution of its three species, has a very homogeneous and unusual flavonoid profile with gossypetin 7-methyl ether as a major constituent, found otherwise only in *Catecolea enodis* in the *Desmocladus* group. It is interesting that "*A. chilensis*" (from Chile) and *A. brownii* (from Victoria, Tasmania and South Australia) have identical aglycone patterns based on gossypetin 7-methyl ether and produce the same unusual glycoside, gossypetin 7-methyl ether 3-glucoside-8-galactoside (or 3-galactoside-8-glucoside) (see Table 3) while "*A. ceramophila*" (from Western Australia) is distinguished by the additional presence of hypo-

Table 5. A summary of culm flavonoids of genera in the *Leptocarpus* group

	No of samples	Flavones Lu	Hyp	Hyp 7ME	Flavonols Qu	Goss	Goss 7ME	Flavonoid SO_4s	Flavone glucuronides
*Leptocarpus**	3	+	+	+	−	−	−	+	+
Hypolaena	(3)	+	+	−	−	−	−	+	−
	(1)	+	−	−	−	−	−	+	−
	(1)	+	+	−	−	−	−	(+)	−
Stenotalis	(1)	+	+	−	+	−	−	+	+
	(1)	+	+	−	−	−	−	+	+
Meeboldina	(4)	+	+	+	−	−	−	+	+
	(3)	+	+	−	−	−	−	+	+
Chaetanthus	(1)	+	+	+	−	−	−	+	+
	(2)	+	+	−	−	−	−	+	+
Apodasmia	(2)	−	−	−	−	−	+	−	−
	(1)	+	+	−	+§	+	+	−	−
Dapsilanthus	(1)	+	+	−	−	−	−	−	+
	(1)	+	+	−	−	−	−	−	+

* *Leptocarpus tenax* is a variable species—in two accessions Lu and Hypolaetin were not detected.
§ Isorhamnetin was also present.

laetin in both instances and luteolin, quercetin and isorhamnetin in one of them.

Dapsilanthus is the only genus limited to the tropics of northern Australia and southern New Guinea and also includes one species from S.E. Asia. Chemically the hypolaetin plus luteolin pattern suggests it is more similar to *Hypolaena* than to *Leptocarpus* and its allies. Within *Hypolaena* there is little chemical support for the incorporation of *Leptocarpus humilis* (*H. humilis*) because it is the only member of the genus to lack hypolaetin, although it does produce luteolin glycosides in common with the other taxa. Since hypolaetin is found in related genera, although somewhat sporadically, its absence from *H. humilis* cannot be regarded as clearly plesiomorphic, although this species shows the primitive feature of relatively large, unreduced tepals. However, since it is appropriately included on other taxonomic grounds, the chemistry does support its separation into its own section "*Homeolaena*" leaving the remaining closely related species in section *Hypolaena*.

It is perhaps easier to consider the taxonomic relationships in the *Leptocarpus* group if some of the flavonoid glycoside evidence is also taken into account. Thus, the summarised aglycone data has been compared with the presence/absence of flavone glucuronides and flavonoid sulphates in Table 5 and the results of a detailed glycoside analysis of representative species of most of the genera are given in Table 3. From this evidence the two most clearly defined genera are *Hypolaena* and *Apodasmia*, which both lack glucuronides but are distinguished from each other by the presence of gossypetin 7-methyl ether in the latter and its absence in the former. Also, in most *Hypolaena* species flavone sulphates are the major flavonoid constituents e.g. hypolaetin 7-sulphate-8-glucoside and luteolin 7-sulphate in *Hypolaena fastigiata*. *Dapsilanthus* on the other hand is distinguished from all the remaining genera by the absence of flavonoid sulphates. *Leptocarpus* is characterised by the presence of hypolaetin 7-methyl ether, again usually as a sulphated glycoside and often as the glucuronide e.g. as the 3′-sulphatogalactoside in *L. tenax* and as the 3′-sulphatoglucuronide in *L.* "*elegans*", where luteolin and chrysoeriol 7,3′-diglucuronide sulphates were also characterised. *Leptocarpus tenax* is chemically variable in that two accessions apparently lack both luteolin and hypolaetin. This may reflect its wide distribution in the south of Western Australia and in eastern Australia from S.E. Queensland to Tasmania and South Australia. The chemical summary of the *Leptocarpus* group in Table 5, clearly shows the variability of two of the other genera, *Meeboldina* and *Chaetanthus* in the presence/absence of hypolaetin 7-methyl ether amongst their species. On the basis of chemical data alone it would be more satisfactory if all the hypolaetin 7-methyl ether producing species in these genera could be retained/included in *Leptocarpus* and the others combined with *Stenotalis* where it is absent, but such groups would be discordant in respect of other features. It should be further noted that "*Meeboldina scariosa*" has an identical two dimensional flavonoid glycoside pattern to "*Leptocarpus diffusus*", suggesting a closer relationship than their inflorescence structures would indicate.

SUMMARY OF RESULTS

The Lepyrodia *Group*

1. The six new *Sporadanthus* species (ex *Lepyrodia*) form a homogeneous chemical group but five other

species which have been retained in *Lepyrodia* have a similar flavonoid pattern.
2. *Lepyrodia* is very heterogeneous with three chemical groups.
3. *Calorophus elongatus* is chemically distinct from *Lepyrodia*, *Sporadanthus* and all other Australian Restionaceae except for one accession of *Empodisma minus*, in producing 5-glycosylated flavonols.

The Winifredia *Group*

4. There is flavonoid evidence to support the isolated position of *Winifredia*.

The Desmocladus *Group*

5. *Empodisma* is clearly separated from both *Calorophus* and *Hypolaena* with which it was formerly confused.
6. *Coleocarya* and *Empodisma* (with the exception of one accession) have similar flavonoid aglycone patterns.
7. *Catacolea* is distinct from other members of the *Desmocladus* group in producing gossypetin 7-methyl ether, otherwise found only in *Apodasmia* (*Leptocarpus* group).
8. There is good flavonoid evidence for the separation of "*Desmocladus quiricanus*", "*D. myriocladus*" and "*D. lateriticus*", which were once treated as one large variable species.
9. There is evidence that *Onychosepalum* is allied to but distinct from *Lepidobolus*.
10. *Kulinia*, with its single rare species, has a unique flavonoid profile amongst Australian Restionaceae.

The Loxocarya *Group*

11. The *Loxocarya* group, which includes most of the original Australian species originally placed in *Restio*, is chemically very diverse with none of the larger genera clearly defined.
12. The new monotypic genera *Guringalia* and *Saropsis* are chemically different from *Baloskion*.
13. *Alexgeorgea* has a unique flavonoid profile.
14. *Taraxis* and *Tyrbastes* have similar floral structure and habit but are chemically distinct.

The Leptocarpus *Group*

15. There is no clear flavonoid distinction between *Leptocarpus*, *Meeboldina* and *Chaetanthus* species.
16. "*Meeboldina scariosa*" and "*Leptocarpus diffusus*" have identical flavonoid glycoside patterns, which differ slightly from those of other species surveyed in the Group.
17. *Apodasmia* is a homogeneous genus with unusual flavonoid profile based on gossypetin 7-methyl ether.

Table 6. Flavonoid comparisons between Restiads of Australia and those of South Africa

Flavonoid character	Percentage frequency in plants Australia*	South Africa†
Flavones		
Luteolin	57	17
Apigenin	1	2
Chrysoeriol	8	5
Tricin	17	0
Hypolaetin	48	0
C-glycosides	16	26
Flavonols		
Myricetin	9	22
Quercetin	30	31
Kaempferol	9	10
Gossypetin	9	5
Gossypetin 7-methyl ether	3	10
Larycitrin	0	24
Syringetin	0	21
Herbacetin 4′-methyl ether	0	7
Quercetin 3-methyl ether	1	0
Isorhamnetin	9	0
Proanthocyanidins	4	88
Sulphated derivatives	27	2

* Based on 115 species surveyed during this work.
† Based on 42 species surveyed earlier [6, 9].

18. *Dapsilanthus* is chemically more similar to *Hypolaena* than to *Leptocarpus*.
19. The flavonoid evidence does not add support for the transfer of *Leptocarpus humilis* to *Hypolaena* but its separation in a monotypic section is supported.

Comparative flavonoid analyses of Australian and South African Restionaceae

As a result of the present work, flavonoid data for most of the Australian Restionaceae have become available. Hence, it is now possible to revise the correlations that clearly exist between flavonoid chemistry and plant geography that were proposed earlier [11]. The percentage of the various flavones, flavonols, proanthocyanidins and sulphated derivatives are shown in Table 6. As can be seen, there are a number of distinctive features which separate the plants of two continents. Australian plants, for example, tend to produce flavones and both luteolin (in 57% of samples) and hypolaetin (in 48%) are characteristic components. By contrast in South African plants, flavonols are regular constituents, with myricetin and its two methyl ethers, larycitrin and syringetin occurring in over a quarter of the plants. The higher frequency of myricetin in African plants (22% compared with

9%) is correlated with a frequent presence of proanthocyanidins (in 88% of sample); proanthocyanidins are rarely present, however, in the Australian sample (see Table 1). Additionally, some individual structures are restricted to plants of one or other continent. Thus, isorhamnetin, tricin and hypolaetin are only found in Australian taxa. It is interesting here that isorhamnetin also occurs in the Anarthriaceae, a Poalean family related to Restionaceae which is also found in Australia. Flavonoids only present in South African plants include larycitrin, syringetin and herbacetin 4′-methyl ether [6, 11]. The widespread occurrence of isorhamnetin in the allied families Anarthriaceae, Hopkinsiaceae, Lyginiaceae and Ecdeiocoleaceae [12] suggests that its absence from African Restionaceae is an advanced feature. On the other hand, the presence of hypolaetin in a considerable proportion of Australian Restionaceae, but not in the *Lepyrodia* and *Winifredia* groups, suggests that its presence represents an advanced feature developed within the Australian members. Overall, then, the differences in flavonoid pattern are to be expected in plants from the same family but from two different continents. They confirm the view that such plants should not be treated together as belonging to the same genera but should be placed systematically in different genera, as in the recent treatment of the Australasian species [7–9].

EXPERIMENTAL

Plant material

Dried culm material was used for all the Restionaceae taxa studied, most of which were collected and verified by two of us (B.G.B. and L.A.S.J.) and for which voucher specimens have been lodged in the National Herbarium of New South Wales, Royal Botanic Gardens, Sydney, Australia (NSW). The remaining accessions, supplied by other collectors, were also verified by B.G.B. and L.A.S.J. and herbarium specimens deposited in NSW.

Identification of culm flavonoids

The flavonoid constituents were extracted from culm tissue in hot 80% MeOH and the concd extracts run two dimensionally in BAW and 15% HOAc on Whatman No. 1 paper to obtain a flavonoid profile for each taxon. Also each direct extract was electrophoresed at pH 4.4 (acetate buffer) and pH 2.2 (HOAc:HCOOH buffer) at 40 V/cm for 2 h to test for the presence of flavonoid glucuronides and flavonoid sulphates, respectively. To facilitate flavonoid aglycone analysis the flavonoid constituents in the MeOH culm extracts were first separated from interfering cinnamic acid and other phenolic constituents by either multiple 2 DPPC in BAW and 15% HOAc or 1 DPPC in 15% HOAc or BAW as appropriate.. The flavonoid spots/bands were cut out, combined and eluted with 80% MeOH to give a partially purified flavonoid fraction for each taxon. The concd eluents were acid hydrolysed and the flavonoid aglycones were identified by comparison with authentic markers using standard procedures.

Flavonoid glycosides

Known glycosides, isolated and purified by standard procedures, were characterised on the basis of UV spectral analysis, R_f and R_t data, acid hydrolysis to aglycone and sugar and where possible by direct comparison with standard markers. Flavone *C*-glycosides were confirmed by 4 h acid hydrolysis with 2 M HCl, extraction into *iso*-amyl alcohol and 2DPC in BAW and 15% HOAc and 1DTLC on cellulose on BAW and H_2O compared with vitexin and isovitexin. HPLC analysis was carried out on a Waters 600 multisolvent delivery system, fitted with a reverse phase Bondapak phenyl column, dimensions 4 mm 1D + 300 mm. HPLC conditions: solvent A = 2% HOAc, solvent B = MeOH:HOAc:H_2O (18:1:1) using the flavonoid glycoside programme 75% A: 25% B → 35% A: 65% B in 23 min in linear mode at 25°, flow rate 1 ml min^{-1} with diode array detection at 260 and 350 nm.

Identification of hypolaetin 7-sulphate-8-glucoside (**1**) *from* Hypolaena fastigiata

R_f and UV spectral data for **1** are given in Tables 7 and 8, respectively. The negative sodium acetate shift indicated that the 7-hydroxyl was substituted and the positive borate shift that the B-ring had two free *ortho* dihydroxy groups. Electrophoretic mobility at pH 2.2 of 2 cm after 2 h and the absence of mobility at pH 4.4 suggested that **1** is sulphated. The detection of glucose after only 5 min acid hydrolysis with 2 M HCl at 100° indicated that it was attached at the 8- rather than the 7-position and the lack of a sodium acetate shift in the intermediate suggested that the 7-hydroxyl was sulphated. This intermediate was mobile at pH 2.2 confirming that it was the 7-sulphate. Acid hydrolysis for: (1) 3 min gave some hypolaetin and a trace of 6-hydroxyluteolin; (2) 10 min gave equal quantities of both aglycones; and (3) 20 min acid hydrolysis gave mainly 6-hydroxyluteolin with a trace of hypolaetin. FABMS of **1** gave a molecular ion at 544 ($C_{21}H_{19}O_{15}S$) requires 544 confirming the structure as hypolaetin with one glucose and one sulphate moiety. The rapid acid hydrolysis of **1** shows that the glucose must be attached to the 8- rather than the 7-hydroxyl (flavone 7-glucosides are relatively resistant to acid hydrolysis) [16] and its co-occurrence with luteolin 7-sulphate supports the location of the sulphate group at the 7-hydroxyl position.

Table 7. R_f and HPLC R_t data for new and unusual glycosides found in the Restionaceae

	Colour UV/NH_3	BAW	Rf × 100 on TLC cellulose in 15% HOAc	H_2O	CAW 1:1	HPLC R_t	Electrophoretic mobility (cm) at pH 2.2	4.4
Flavones								
Hypolaetin								
7-SO_4-8-Glc* (**1**)	Dk/Dk	29	27	nd	nd	19.05§	2.0	0
7-Glur SO_4† (**2**)	Dk/Dk	18	24	73	0	nd	2.0	2.6
7-Glc SO_4‡ (**3**)	Dk/Dk	27	05	51	0	nd	1.6	0
7-Gal SO_4‡ (**3**)								
Hypolaetin 7 ME								
3′-Glur SO_4‡ (**4**)	Dk/Dk	27	05	51	17	nd	0.3	0.5
3′-Gal SO_4§ (**6**)	Dk/Dk	24	14	32	nd	nd	1.75	0
Hypolaetin 7,3′-DIME								
4′-Glc‡ (**5**)	Dk/Dk	27	05	51	42	nd	0	0
Luteolin di-*C*-glyc¶	Dk/Y	12	14	05	03	nd	—	—
Apigenin di-*C*-glyc¶	Dk/Y	14	26	10	06	nd	—	—
Flavonols								
Myricetin acylated 3-Glc‡‡ (**6**)	Dk/Y	12	22	49	01	—	—	1.4
Quercetin 3ME								
5-Glc‖ (**7**)	B/Y	45	21	02	08	15.67	—	—
5-Glc-3′-SO_4‖ (**8**)	B/Y	31	56	71	0	11.63	1.6	—
Gossypetin								
3-Glc**	Dk/Dk	46	26 In 50% HOAc	36 In forestal	39	nd	—	—
7-Glc**	Dk/Dk	37	37	53	24			
Gossypetin 7ME		38	30	05	28	nd	—	—
3-Glc-8-Gal†† (**9**) (or 3-Gal-8-Glc)	Dk/Dk							
3-Gal-8-Glc [6]	Dk/Dk	32	30	09	nd	nd	—	—

* from *Hypolaena fastigiata*.
† from "*Meeboldina thysanantha*".
‡ from *Leptocarpus elegans*.
§ from *Leptocarpus tenax*.
¶ from *Winifredia sola*.
‖ from *Calorophus elongatus*.
** from *Eurychorda complanata*.
†† from *Apodasmia brownii*.
‡‡ from *Lepyrodia anarthria*.
The HPLC programme for this glycoside differed from that given in the Experimental in that solvent A was H_2O not 2% HOAc. Therefore the R_t is slightly longer by comparison.

Identification of hypolaetin 7-sulphatoglucuronide (**2**) *from* "Meeboldina thysanantha"

R_f and UV spectral data for compound **2** are listed in Tables 7 and 8, respectively. The very high mobility of **2** in H_2O (R_f 73) and electrophoretic mobility at both pH 2.2 (2 cm) and pH 4.4 (2.6) and low R_f in BAW (18) suggested it to be a sulphated glucuronide. Acid hydrolysis with 2 M HCl at 100° for 40 min gave a mixture of hypolaetin and 6-hydroxyluteolin and glucuronic acid. The negative sodium acetate shift and positive borate shift indicated that both the glucuronic acid and sulphate were attached at the 7-hydroxyl and that the 3′ and 4′-positions were free. There was insufficient sample for MS studies to confirm the number of sugar and sulphate moieties, but R_f data are consistent with its formulation as hypolaetin 7-sulphatoglucuronide.

Identification of hypolaetin 7-sulphatoglucoside and 7-sulphatogalactoside (**3**), *hypolaetin 7-methyl ether 3′-sulphatoglucuronide* (**4**) *and hypolaetin 7,3′-dimethyl ether 4′-glucoside* (**5**) *from* "Leptocarpus elegans"

R_f and UV spectral data for **3**–**5** are presented in Tables 7 and 8, respectively. Compound **3** gave a mixture of hypolaetin and 6-hydroxyluteolin after acid hydrolysis for 40 min together with glucose and galactose. Compound **4** gave hypolaetin 7-methyl ether and glucuronic acid after 40 min acid hydrolysis while **5** gave a hypolaetin dimethyl ether and a trace

Table 8. UV spectral data for new and unusual glycosides found in the Restionaceae

Flavonoid	λ MeOH max	+NaOAc	+H_3BO_3	+HaOH	+$AlCl_3$	+$AlCl_3$/HCl	HPLC λ max
Flavones							
Hypolaetin							
7-SO_4-8-Glc* (**1**)	276, 255′, 346	274, 255′, 351	264, 378	nd	276, 356, 415′	277, 355, 415′	nd
7-Glur SO_4† (**2**)	233, 276, 343	265, 376	266, 377	345, 391	274, 315, 434	243, 274, 354	nd
70Glc SO_4‡ (**3**) / 7-Gal SO_4‡ (**3**)	272, 340	272, 342	271, 349	nd	nd	nd	nd
Hypolaetin 7ME *isomerised to 6 OH Lu 7ME	272, 280′, 340	272, 280′, 364	264, 272, 289′, 364′	nd	nd	nd	nd
3′-Glur SO_4‡(**4**)	274, 339	274, 340	274, 341	nd	nd	nd	nd
3′-Gal SO_4§ (**6**)	252, 271, 301, 344	252, 271	346	404	nd	nd	nd
Hypolaetin 7, 3′DIME							
4-Glc?‡ (**5**)	272, 333	272, 333	272, 333	nd	nd	nd	nd
Luteolin di-*C*-glyc¶	272, 348	282, 403	270, 368	245, 282	nd	nd	nd
Apigenin di-*C*-glyc¶	274, 334	282, 389	276, 334	247, 283, 335, 401	nd	nd	nd
Flavonols							
Myricetin							
acylated 3-Glc‡‡ (**6**)	263, 363	273, 389	261, 384	279, 325, 418	262, 403	269, 364	nd
Quercetin 3ME							
5-Glc‖ (**7**)	255, 353	268, 379	260, 372	267, 401	245, 378	251, 352	252, 352
5-Glc-3′-SO_4‖ (**8**)	262, 338	270, 388	264, 343	267, 393	256, 342	256, 339	262, 344
Gossypetin							
3-Glc**	261, 345, 380	265, 353, 394	266, 394	268, 369	nd	nd	nd
7-Glc**	261, 346, 386	262, 348, 394	266, 398	269, 363	nd	nd	nd
Gossypetin 7ME							
3-Gal-8-Glc†† (**9**) (or 3-Gal-8-Glc)	278, 307, 345	276, 347, 400	269, 386	261, 368 stable	283, 439	286, 318′, 360	nd
3-Gal-8-Glc from *Apodasmia chilensis*	262, 276, 344, 372	262, 276, 354, 374	387	slowly decomp. 384	280, 286, 364, 422	nd	nd
3-Gal-8-Glc from *Erigonum nudum* (Lit data [16])	260, 273, 308, 350	258′, 272	292	403	452	nd	nd

* from *Hypolaena fastigiata.*
† from "*Meeboldina thysanantha*".
‡ from *Leptocarpus elegans.*
§ from *Leptocarpus tenax.*
¶ from *Winifredia sola.*
‖ from *Calorophus elongatus.*
** from *Eurychorda complanata.*
†† from *Apodasmia brownii.*
‡‡ from *Lepyrodia anarthria.*

of glucose. Both **3** and **4** were mobile on electrophoresis at pH 2.2 (1.6 and 0.3 cm, resp.) while **4** was also mobile at pH 4.4 (0.5 cm). The absence of a sodium acetate shift and the presence of a positive borate shift in **3** suggested that both the sugar and sulphate moieties were attached at the 7-hydroxyl. Compound **3** is thus a mixture of hypolaetin 7- sulphatoglucoside and 7-sulphatogalactoside. Both **4** and **5** gave negative sodium acetate and borate shifts in their UV spectra. Compound **4** was tentatively identified as hypolaetin 7-methyl ether 3′-sulphatoglucuronide but there was insufficient material to carry out an alkaline shift to rule out the possibility of the 4′-sulphatoglucuronide isomer. Similarly from the available data **5** is probably hypolaetin 7,3′-dimethyl ether 4′-glucoside but the positions of the methoxyl and glucose on the B ring are unproven.

Identification of hypolaetin 7-methyl ether 3′-sulphatogalactoside (**6**) *from* Leptocarpus tenax

R_f and UV spectral data for **6** are given in Table 7 and 8. Compound **6** gave hypolaetin 7-methyl ether and galactose on acid hydrolysis and was mobile at pH 2.2. the negative sodium acetate shift indicated the 7-position was substituted and the high intensity alkaline shift that the 4′-hydroxyl was free. The glycoside (**6**) gave no borate shift but the aglycone gave

a positive shift. Therefore, the 3′-hydroxyl must be substituted. EIMS of the aglycone **6a** gave a molecular ion at 316 ($C_{16}H_{12}O_7$, requires 316) and a B-ring fragment (134 mn) indicating 3′,4′-dihydroxylation, which is consistent with the structure of either 6- or 8-hydroxyluteolin 7-methyl ether.

The absence of an M-15 ion in MS of **6a** rules out methylation at the 5- or 8-positions. The UV spectrum of **6a** is in accord with 8-hydroxylation, with maxima at 250, 270 and 350 nm. Evidence for 7-*O*-methylation is based on the lack of sodium acetate shift in **6** (see above) and also from the relative HPLC retention times. Thus, 7-*O*-methylation in the kaempferol and quercetin series reduces mobility much more than *O*-methylation elsewhere in the flavonoid molecule [17]. This is also true of luteolin (R_t 5.62 min) compared to its 7-methyl ether (R_t 9.28 min). Very similar differences separate hypolaetin (R_t 4.56 min) from its presumed 7-methyl ether **6a** (R_t 7.15 min). Hence **6a** would appear to be hypolaetin 7-methyl ether and **6** is the 3′-sulphatoglucoside.

Identification of quercetin 3-methyl ether 5-glucoside (**7**) *and 5-glucoside-3′-sulphate* (**8**) *from* Calorophus elongatus

Both **7** and **8** appeared blue to yellow in UV light with NH_3 and gave quercetin 3-methyl ether and glucose on acid hydrolysis. However, **8** was mobile at pH 2.2, i.e. was sulphated, and **7** was not mobile. This is also reflected in the high mobility of **8** on TLC in water and low mobility in BAW compared with **7** (Table 7). The UV spectral analysis (Table 8) suggested that **7** had free 7,3′ and 4′ hydroxyls from positive sodium acetate and boric acid shifts, while the positive $AlCl_3$ shift, which returned to the neutral value on addition of 2 M HCl indicated that the 5-hydroxyl was substituted. Therefore, **7** is identified as quercetin 3-methyl ether 5-glucoside.

This was confirmed by FAB-MS, which gave a molecular ion at 478 ($C_{22}H_{22}O_{12}$ requires 478) and a fragment ion at 316 corresponding to the quercetin 3-methyl ether. Compound **8** also gave a positive sodium acetate shift but no borate shift. The strong alkaline shift of high intensity indicated that the 4′-position was free, suggesting that the 3′-hydroxyl must be substituted. The absence of an $AlCl_3$ shift and blue to yellow colour in UV/NH_3 also showed that the 5-hydroxyl was substituted. Negative FAB-MS of **8** gave 557 i.e. a molecular ion at 558 confirming the presence of one glucose and one sulphate group on the quercetin 3-methyl ether aglycone. The structure of **8** is therefore either quercetin 3-methyl ether 5-glucoside-3′-sulphate or its isomer but probably the former because of its co-occurrence with the 5-glucoside (**7**). Attempts to selectively remove the sulphate group from **8** by 5 min hydrolysis with sulphatase at pH 5 failed, since such treatment of **7** and **8** gave only quercetin 3-methyl ether and no intermediate suggesting and confirming the position of the glucoside at the 5-hydroxyl from where it is very easily hydrolysed.

The identification of gossypetin 7-methyl ether 3-galactoside-8-glucoside (**9**) *from* Apodasmia brownii

R_f HPLC R_t and UV spectral data for **9** are given in Tables 7 and 8. Acid hydrolysis gave gossypetin 7-methyl ether and glucose and galactose in equal amount. The aglycone was identified by comparison (R_f and UV spectral analysis) with authentic markers of gossypetin 7- and 8-methyl ethers. The absence of a NaOAc shift confirmed the methoxyl at the 7-position. The dark to yellow colour of the glycoside suggested that a sugar was attached at both the 3- and 8-hydroxyls, however, it was not possible to determine whether **9** was a 3-Gal-8-Glc, or 3-Glc-8-Glc or a mixture of the two. However, an identical glycoside has been identified in *A. chilensis* from Chile (J. B. Harborne, unpub. results) and the UV, R_f and MS data are in agreement with that of gossypetin 7-methyl ether 3-Gal-8-Glc characterised in *Eriogonum nudum* Dougl. ex Benth. subsp. *saxicola* (Heller) Munz. [18].

Partial characterisation of an acylated myricetin 3-glucoside (**6**) *from* Lepyrodia anarthria

R_f and UV spectral data for **6** are given in Tables 7 and 8. Acid hydrolysis gave myricetin and glucose. Alkaline hydrolysis gave myricetin 3-glucoside but no acyl group could be detected. However, its mobility on electrophoresis at pH 4.4 suggested that **6** is acylated. There was insufficient compound to give a good FAB-MS.

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