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CORRELATIONS BETWEEN PHENOLIC PATTERNS AND TRIBAL CLASSIFICATION IN THE FAMILY IRIDACEAE

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Key Word Index—*Iris*; Iridaceae; phenolics; flavonoids; quinones; xanthones; biflavonoids; anthocyanins; chemotaxonomy.

Abstract—A survey of 255 species from 57 genera representing all the tribes in the Iridaceae has indicated considerable heterogeneity in the distribution of flavonoids and other phenolics in the leaves. Thus the Iridoideae and Tigrideae can be distinguished from other tribes by the regular presence of mangiferin, whereas the Trimezieae and Sisyrincheae can be separated by the absence of flavonols. Again, the Aristeae and Nivenieae are distinguished by the presence of plumbagin, although this quinone does occur in isolated instances in two other tribes. These two tribes also rarely have glycoflavones, which are otherwise almost universally present. Members of the Watsonieae are separated by the fact that only flavonols are present, while the Ixieae have a number of distinctive flavones, notably tricin, acacetin, 6-hydroxyluteolin and scutellarein derivatives. *Isophysis tasmanica*, the only taxon of the Isophysidoideae, is unusual in having the biflavonoids, amentoflavone and dihydroamentoflavone, with only traces of glycosylflavones. Anthocyanin patterns in the flowers also vary at the tribal level, with acylated pigments being apparently confined to the Irideae. Syringetin, larycitrin and myricetin 3-galactosides were identified in flowers of *Gladiolus tristis* (Ixieae), whereas glycoflavones were found to predominate in flowers of *Iris* species (Irideae). These varying patterns may be helpful in placing uncertain genera into their correct tribes. The phenolic pattern of the family as a whole is heterogeneous and shows only a few chemical links with any neighbouring families.

INTRODUCTION

As the culmination of a chemotaxonomic survey of flavonoids and related phenolics in families of the monocots [1, 2] we now report the results of investigating the Iridaceae. This ornamental family of about 1500 species and 85 genera is most richly represented in South Africa and tropical America but has an almost worldwide distribution. The genus *Iris*, for example, inhabits the northern hemisphere with a centre of origin in Asia. A few genera show markedly disjunct distributions in different continents, notably *Libertia* and *Orthrosanthus* (Australia and S. America) and *Dietes* (Africa and Lord Howe Island). Taxonomically the family is related to the Liliaceae (*sensu stricto* [3]) and Colchicaceae but its exact affinities are presently obscure. In a recent treatment Goldblatt [4, 5 and unpublished work] has divided the family into three subfamilies: the monotypic Isophysidoideae and the Iridoideae and Ixioideae, which are further divided into five and two tribes, respectively (see Table 1). The positioning of genera within the tribes however is still under active investigation.

Although the chemistry of the family has been reasonably fully investigated [6], relatively few surveys have been undertaken. Thus, various *meta*-carboxy substituted aromatic amino acids and glutamyl peptides have been reported widely in the subfamily Iridoideae, but not in the other subfamilies [7]. The pioneering survey of Bate-Smith of leaf phenolics showed that a wider range of constituents were present than in any other neighbouring group [8]. The major flavonoids detected by him were flavone *C*-glycosides and the flavonols, kaempferol and quercetin. Additionally, the unusual *C*-glucosylxanthone, mangiferin, was found to be characteristic of certain groups of *Iris* species, especially section *Pogoniris* [9]. *Iris* is also unusual in producing isoflavones, especially in rhizomes, although these compounds have only so far been positively identified in ten species and in the closely related *Belamcanda chinensis* [10]. Floral tissues of some ten genera have yielded a range of anthocyanin pigments [11] and *Iris* flowers have furnished *C*-glycosylflavones with 7- and/or 4′-methylation [12] and occasionally with additional acetylation [13].

Some parts of the present investigation have been recorded briefly in two earlier papers [14, 15]. Here we provide full details of a survey of 255 species representing 57 genera.

RESULTS

Leaf constituents

The results of a leaf phenolic survey of 255 species of the Iridaceae are presented in Table 1. Both fresh and herbarium material was used. The data refer largely to flavonoid aglycones identified in leaf tissue after acid hydrolysis by direct comparison with authentic markers. The results were confirmed by 2D-PC of direct leaf extracts and by the identification of flavonoid glycosides in representative species (Table 2). Flavone *C*-glycosides were confirmed by their resistance to four hour acid

Table 1. A leaf flavonoid survey of the Iridaceae

Subfamily* tribe, species	Flavone C-glycosides	Flavonols	Others	Plant source†	Accession number or collectors name or number
Isophysidoideae					
Isophysis tasmanica (Hook. f.) T. Moore	(+)	–	Amentoflavone, 2,3-dihydroamentoflavone + unknown biflavonoid	NSW	I. Olsen 60
Iridoideae					
Aristeae					
Aristea alata Baker	–	Qu, Km	Plumbagin	K	084–81.01253
A. compressa Buchinger ex Krauss	–	Qu, Km	Plumbagin	K	080–61.08002
A. ecklonii Baker	–	Qu, Km	Plumbagin	R	ex John Ingham
A. ensifolia Muir	–	Qu, Km	Plumbagin	K	039–64.03902
A. lugens Hort. ex Steud.	–	Qu(Km), (Isorh)	Plumbagin	M	
A. platycaulis Baker	–	–	Plumbagin	K	000–69.52032
A. singularis H. Weim.	–	Qu, Km	Plumbagin	MO	P. Goldblatt 7253
Klattia partita Baker var. *flava* Lewis	–	Qu, Km, My, Isorh	Dk/Dk unident.	MO	P. Goldblatt 6920
K. stokoei L. Guthrie	–	Qu, Km, My, (Isorh)		SAM, RNG	J. P. Rourke 1821
Nivenia fruticosa (L. f.) Baker	–	Qu, Km, Isorh	–	MO	Esterhuysen 36149
N. stokoei N. E. Brown	–	Qu, My	2 Dk/Dk unident.	SAM, RNG	D. Snijman 838
Nivenia sp. nov.	–	Qu, Km	ProDp	MO	P. Goldblatt 7178
Patersonia fragilis (Labill.) Asch. & Graebn.	–	Qu, Isorh	ProCy, ProDp	NSW	P. Hind 3582
P. glabrata R. Br.	+	–	ProCy, Amentoflavone	NSW	R. Coveny 11831 & C. Miller
	+	–	Amentoflavone	NSW	R. Coveny 11834 & C. Miller
	+	–	Amentoflavone, ProCy, ProDp	NSW	R. Coveny 12099
	+	–	Amentoflavone	NSW	R. Coveny 12109 & C. Dunn
P. glabrata R. Br.	–	Qu, Isorh	Tricin, ProCy	NSW	P. Hind 3557
P. longifolia R. Br.	–	My(Qu), (Isorh)	(ProCy)	NSW	R. Coveny 11835 & C. Miller
P. longiscapa Sweet	–	Qu, Isorh	–	M	
P. occidentalis R. Br.	–	Qu, Km, My, Isorh	ProDp, Dk/Dk unident.	K	149–83.01737
P. sericea R. Br.	–	Qu, Isorh, My	(ProCy)	NSW	R. Coveny 11837 & C. Miller
	–	Qu, Isorh, My	2 Dk/Dk unident.	NSW	P. Hind 3544
	–	Qu, Isorh, My	ProCy, ProDp	NSW	R. Coveny 12098
Witsenia maura Thunb.	–	Qu, Isorh, My	ProDp, 2 Dk/Dk unident.	MO	Orchard 35
	–	Qu, Isorh, My	2 Dk/Dk unident.	SAM, RNG	D. Snijman 839
Irideae					
Bobartia macrospatha subsp. *anceps* (Baker) Strid	+	–	–	MO	Lewis 5929
Dietes bicolor (Steud.) Sweet ex Klatt	+	Qu, Km	ProCy	M	
D. flavida Oberm.	+‡	–	–	K	411–67.41114
D. grandiflora N. E. Br.	+‡	–	–	K	275–67.27508
D. robinsoniana (F. Muell.) Klatt	+	–	–	K	000–73.19994
D. vegeta (L.) N. E. Br.	+	–	ProCy, ProDp	K	286–73.06324
Diplarrhena latifolia Benth.	+	–	–	K	241–80.02383

D. moraea Labill.	+	–	–	K§	Cult. Wakehurst Gardens W161
Galaxia alba Lewis	+	–	–	K	306–83.0382
Gynandriris australis Goldbl.	+	–	Mangiferin, Isomangiferin	K	306–83.03483
G. setifolia (L.f.) R. Foster	+‡	–	Mangiferin, Isomangiferin	K	312–77.02410
G. sisyrinchium (L.f.) Parl	+	–	–	K	22–55.22003
Hermodactylis tuberosus (L.) Miller	+	–	–	R	79042
	+	–	Tricin	K	314–72.02991
Hexaglottis virgata (Jacq.) Sweet	–	–	Tricin	K	306–83.03478
	+	–	–	M	
Homeria collina (Thunb.) Salisb.	+	–	Tricin	R	801031
	–	–	Lu, Tricin	K	259–77.02014
H. flavescens Goldbl.	–	–	–	K	306–83.03481
H. lilacina L.	–	–	unident. aglycones	K	259–77.02007
H. longistyla Goldbl.	+‡	Qu, Km	Tricin	K	429–82.04644
H. ochroleuca Salisb.	–	–	Tricin	K	306–83.03474
H. patens Goldbl.	–	–	Tricin	K	306–83.03479
Subgenus *Iris*					
Section *Iris*					
Iris albertii Regel	+	–	Mangiferin, Isomangiferin	R	800777
I. albicans Lange	+	–	–	R	820539
I. aphylla L.	–	–	Mangiferin, Isomangiferin	R	780363
I. germanica L.	+	–	Mangiferin‖, Isomangiferin Mangiferin *O*-glyc.	K	000–69.19197
	+	–	Mangiferin‖, Isomangiferin	R	780937
I. lutescens Lam.	+	–	Mangiferin, Isomangiferin	R	761287
	+	–	Mangiferin, Isomangiferin	R	770376
	+	–	Mangiferin§, Isomangiferin	K	603–58.60301
I. lutescens Lam. yellow form	+	–	Mangiferin‖, Isomangiferin Mangiferin *O*-glyc.	K	000–69.19184
I. lutescens Lam. var. *alba*	+	–	Mangiferin§, Isomangiferin	K	000–69.19180
I. pallida subsp. *cengialtii* (Ambr.) Foster	+	–	Mangiferin, Isomangiferin	R	820541 Mathew 403
I. pseudopumila Tineo	+	–	Mangiferin	R	840570 Akeroyd, Jury, Miles & Rumsey Sicily 3638
I. pumila L.	+	–	Mangiferin‖	R	20002 Jugoslavia
I. reichenbachii Heuffel	+	–	Mangiferin‖, Isomangiferin Dk/Dk aglycone	K	261–40.26104
I. × *sambucina*	+‡	–	Mangiferin§, Isomangiferin 2 Mangiferin *O*-glycosides	K	261–40.26105
I. × *squalens* L.	+	–	Mangiferin‖, Isomangiferin Mangiferin *O*-glycosides	K	000–69.19223
I. subbiflora Brot.	+	–	Mangiferin, Isomangiferin	K	216–72.01907
I. suaveolens Boissier & Reuter	+	–	Mangiferin, Isomangiferin	S	
I. trojana Kerner ex Stapf.	+	–	Mangiferin‖, Isomangiferin	K	000–69.19226
I. variegata L.	–	–	Mangiferin‖, Isomangiferin Mangiferin *O*-glyc.	R	790898

Table 1. (*Continued*)

Subfamily* tribe, species	Flavone C-glycosides	Flavonols	Others	Plant source†	Accession number or collectors name or number
Subgenus *Iris*					
Section *Psammiris*					
Iris humilis Georgi	+	Qu	Mangiferin	R	820195
Subgenus *Iris*					
Section *Regelia*					
I. hoogiana Dykes	+	–	Mangiferin§, Isomangiferin, Mangiferin *O*-glyc.	K	000–73.18765
Subgenus *Limniris*					
Section *Lophiris*					
Iris confusa Sealy	+‡	–	–	R	Mathew 403
I. gracilipes A. Gray	+‡	–	–	R	
I. japonica Thunb.	+	–	–	R	810887
	+	–	–	S	
I. lacustris Nuttall	+‡	–	–	S	
I. milesii Foster	+	–	–	K	613–68.61301
I. tectorum Maxim.	+‡	–	C/B negatively charged compound	R	800800
Subgenus *Limniris*	+				
Section *Limniris*					
Series *Ruthenicae*					
I. ruthenica Ker Gawl.	+	–	–	R	781508
Series *Tripetalae*					
I. setosa Pall. ex Link	+	–	Mangiferin§, Isomangiferin	R	780947
I. setosa subsp. *canadensis* (M. Foster) Hulten	+	–	Mangiferin§, Isomangiferin	R	790191
Section *Limniris*					
Series *Sibiricae*					
Iris chrysographes Dykes	+	–	(ProCy) (ProDp)	R	830758
	+	–	–	R	830759
	+	–	(ProCy) (ProDp)	R	830761
I. clarkei Baker	+	–	ProCy ProDp	R	830763
I. delavayi Micheli	+	My, Qu	–	R	830765
	+	My, Qu	ProCy	R	830764
	+	My, Qu	(ProCy) (ProDp)	R	830765
I. forrestii Dykes	+	(My) (Qu)	–	R	830766
I. sanguinea Hornem. ex Donn	+	My, Qu	Dk + C/B negatively charged compounds	R	750547
	+	My, Qu	–	S	
	+	My, Qu	–	R	810904
	+	(My) (Qu)	–	K	236–77.01819
I. sibirica L.	+	My, Qu	–	R	830767 Davis & Hedge
	+	My, Qu	–	R	810403
	+‡	My, Qu	–	R	790593
	+‡	My, Qu	–	K	490–51.49003

Subgenus *Limniris*					
Series *Californicae*					
I. douglasiana Herbert	+‡	Qu, Km, Isorh	ProCy	R	790899
I. innominata Henderson	+‡	Qu	–	R	760758
I. macrosiphon Torrey	+‡	My, Qu	–	R	801003
I. tenax Douglas ex Lindley	+	–	–	S	Det. S. Linnegar
	+	–	–	K	000–69.1224
Series *Longipetalae*					
I. missouriensis Nuttall	+‡	–	–	K	180–69.01410
Series *Laevigatae*					
I. ensata Thunb.	+	–	(Mangiferin) (Isomangiferin)	R	850069
	+‡	–	Mangiferin‖	K	468–70.04472
	+‡	–	(Mangiferin)	R	781506
I. pseudoacorus L.	+	–	Mangiferin‖, Isomangiferin, Mangiferin *O*-glyc.	H	
I. versicolor L. var. *kermesina*	+	–	Mangiferin, Isomangiferin	R	780958
I. virginica var. *shrevei* (Small) Anders	+	–	(Mangiferin) (Isomangiferin)	K	589–66.58901
Series *Hexagonae*					
I. fulva Ker-Gawl.	+‡	–	–	R	780931
Series *Spuriae*					
Iris graminea L.	+	(My) (Qu)	–	R	311122
	+	–	ProCy	S	
I. graminea var. *pseudocyperus* (Schur.) Beck.	+	–	ProCy	S	
I. monnieri DC.	+‡	–	ProCy	S	
I. orientalis Miller	+‡	–	ProCy	S	
I. sintenisii Janka	+	Qu	–	R	850306
I. spuria subsp. *halophila* (Pall.) Mathew & Wendelbo	+	–	B/G & C/B negatively charged compounds	R	750544
I. spuria subsp. *sogdiana* (Bunge) Mathew	+	–	–	R	760868
Series *Foetidissimae*					
I. foetidissima L.	+‡	–	–	R	770194
I. foetidissima L.	+‡	–	–	R	770194
I. foetidissima L. (yellow form)	+‡	–	–	R	780930
I. foetidissima L. var. *variegata*	+‡	–	–	R	
Series *Ensatae*					
I. lactea Pallas	+‡	–	Mangiferin‖	K	435–57.43501
	+	–	Mangiferin‖, Isomangiferin	R	780939
Series *Unguiculares*					
Iris lazica Alboff	+	–	Mangiferin, Isomangiferin B/G negatively charged compound	R	780957
I. unguicularis Poir. cv. 'Mary Bernard'	+	–	Mangiferin, Isomangiferin	R	800234
I. unguicularis Poir. cv. 'Cecilia Christy-Miller'	+	–	Isomangiferin, C/B & B/G negatively charged compounds	R	760539
Subgenus *Xiphium*					
Iris filifolia Boiss.	+	–	–	R	771082

Table 1. (*Continued*)

Subfamily* tribe, species	Flavone C-glycosides	Flavonols	Others	Plant source†	Accession number or collectors name or number
I. latifolia Miller	+	–	–	R	810224
	+	–	–	S	
	+	–	–	R	810232
	+	–	–	R	810224
I. tingitana Boiss. & Reut.	+	–	–	R	771083
Iris sp. (possible hybrid of *I. tingitana*)	+	–	–	S	
Subgenus *Hermodactyloides*					
Iris histrioides (G. F. Wilson) S. Arnott 'Major'	+	–	Mangiferin, Isomangiferin	R	790422
I. reticulata M. Beib.	+	–	(Mangiferin) (Isomangiferin)	R	751315
	+	–	–	S	
Moraea aristata (de la Roche) Asch. & Graebn.	–	–	Dk/Dk unident.	K	360–73.04789
M. bellendenii N. E. Brown	–	–	Tricin	M	
	–	–	Tricin	K	360–73.04790 commercial stock
M. ciliata (L.f.) Ker-Gawl.	–	Km	–	K	259–77.02005
M. fugax (de la Roche) Jacq.	–	My, Qu	ProDp	R	840139
M. neopavonia R. Foster	–	–	Dk/Dk unident.	K	259–77.02009
M. polyanthos L.f.	–	–	unident, aglycones	K	259–77.2007
M. polystachya (L.f.) Ker-Gawl.	+	–	–	M	
M. tricuspidata (L.f.) G. Lewis	–	–	Tricin	K	556–69.04881
M. unguiculata Ker-Gawl.	–	–	Dk/Dk unident.	K	306–83.03475
M. villosa Ker-Gawl.	–	–	Dk/Dk unident.	K	306–83.03477
Sisyrinchieae					
Libertia chinensis Klotzsch ex Baker	+	–	(Lu) (Ap) ProCy, ProDp	K	000–69.52031
L. ixioides Forst. fil.	+	–	–	K	204–73.01840
	+	–	–	R	800926
L. peregrinans Ckn. et Allan	+	–	ProCy	K	207–78.02199
L. sessiliflora (Poeppig) Skottsb.	+	–	–	M	
Libertia sp.	+	–	ProCy	D	
Orthrosanthus chimiboracensis Baker	+‡	–	–	K	236–77.01837
O. chimiboracensis Baker var. *exsertus*	+‡	–	Dk/Dk unident.	K	263–78.02716
O. multiflorus Sweet	+‡	–	Dk/Dk unident.	K**	RBG H1213/7018
O. nigrorhynchus Rusby	+	–	Dk/Dk unident.	MO	Solomon & Beck 6633
Orthrosanthus sp.	+	–	Dk/Dk unident.	M	J. Ratinsky OSPP-24
Phaiophleps acaule (Klatt) R. Foster	+	–	Plumbagin	MO	J. C. Solomon 13032
P. biflorus (Thunb.) R. Foster subsp. *biflorus*	–	–	Lu	RNG	Roivainen 1036
P. biflorus subsp. *lyckholmii* (Dusen) Moore & Doggett	+	–	–	RNG	T.B.P.A. 2635
Sisyrinchium bellum (white form) S. Wats.	+	–	–	R	751250
S. bermudianum L.	+	–	–	K	424–83.05370

S. boreale J. K. Henry	+	–	–	M	8438
S. brachypus (Bickn.) J. Henry	+	–	Plumbagin	K	473–57.47301
S. californicum (Ker-Gawl.) Dryander	+	–	Plumbagin + another quinone	K	424–83.05371
	+	–	Plumbagin	RNG	S. L. Jury, F. J. Rumsey & D. A. Webb 4809
S. chilense Hook.	+	–	–	K	402–72.03697
S. convolutum Nocca	+‡	–	–	K	262–81.03137
S. cuspidatum Poepp.	+	–	–	K	393–67.39312
S. depauperatum Phil.	+	–	–	K	424–83.05375
S. elmeri var. *lilium*	(+)	–	–	K	185–7701519
S. filifolium Gaudich.	+	–	–	K	134–79.01290
S. graminifolium Lindl.	+‡	–	–	M	M 8416
S. idahoense Bickn.	+	–	–	K	007–77.00015
S. iridifolium H.B. & K.	+	–	–	M	8418
S. longipes (Bicknell) Kearney	+	–	–	K	312–83.03744
S. macounii Bickn.	+	–	–	K	424–83.05374
S. macrocarpum Hieron	+	–	–	K	283–74.02337
S. nudicaule Phil.	+	–	–	M	8426
S. striatum Smith	+	–	–	S	
S. tenuifolium H.B. & K.	+	–	–	K	312–83.03722
S. tinctorium H.B. & K.	+	–	–	K	473–69.09279
Sisyrinchium 'Balls mauve'	+	–	–	K	424–83.05373
Solenomelus pedunculatus Miers	+	–	–	MO	Worth & Morrison 16452
S. sisyrinchium (Griseb.) Pax ex Diels	+	–	–	K	153–77.01304
Tapeinia pumila (Forst. f.) Baillon	+	–	ProCy, ProDp	MO	D. M. Moore 2728
Tigrideae					
Calydorea speciosa Herb.	+	–	Tricin ProCy 2 Dk/Y negatively charged compounds	K	108–73.00805
Cardiostigma mexicanum (R. Foster) Ravenna	+‡	–	–	K	312–83.03746
	+‡	–	–	K	312–83.03758
Cipura flava Ravenna	+	Km	–	MO	Irwin, Maxwell & Wasshausen 18503
C. paludosa Aubl.	+	–	1 Dk negatively charged compound	K	306–83.03464
	+	–	1 Dk negatively charged compound	K	312–83.03651
Cypella herberbii Herb.	–	Isorh	B/B compound	R	840146
C. lauthalii (Kuntz.) R. C. Foster	+	-	ProCy, Dk/Y negatively charged compound	M	
Cypella sp.	+	–	Dk/Dk unident.	K	400–76.06049
Eleutherine bulbosa (Miller) Urb.	+	–	Mangiferin, Isomangiferin, 1 Dk & 1 Y negatively charged compound	K	312–83.03664
	+	–	Mangiferin, Isomangiferin 1 Dk & 1 Y negatively charged compound	K	312–83.03666
Ennealophus boliviensis (Baker) Ravenna	+	–	Mangiferin	MO	Solomon 9972
Gelasine azurea Herb.	–	–	Mangiferin, Isomangiferin 1 Dk & 1 Y negatively charged compound	K	306–83.03471
Herbertia lahue (Molina) Goldbl.	+	–	Xanthone? (bright blue)	K	306–83.03469
H. pulchella Sweet	+‡	–	–	M	

Table 1. (*Continued*)

Subfamily* tribe, species	Flavone C-glycorides	Flavonols	Others	Plant source†	Accession number or collectors name or number
Rigidella orthantha Lem.	+	–	Mangiferin, Isomangiferin	K	312–83.03569
	+	–	Mangiferin, Isomangiferin	K	312–83.03528
Rigidella sp.	+	–	Mangiferin, Isomangiferin	K	312–83.03568
Tigridia alpestris Molseed	+	–	Mangiferin, Mangiferin *O*-Glyc, O/Y negatively charged compound	K	312–83.03880
	+	–	Mangiferin, Mangiferin *O*-Glyc.	K	312–83.03883
T. meleagris Nichols.	+	–	–	K	312–83.03768
	+	–	–	K	312–83.03762
T. pavonia Ker-Gawl.	+	–	ProCy, Dk negatively charged compound	K	312–83.03557
	+	–	2 Dk & 1 Dk/Y negatively charged compound	K	312–83.03621
Tigridia sp.	+	–	Mangiferin, Mangiferin *O*-Glyc.	K	312–83.03875
Tigridia sp.	+	–	Mangiferin, Mangiferin *O*-Glyc.	K	312–83.03891
Tigridia sp.	+	–	Mangiferin, Mangiferin *O*-Glyc.	K	312–83.03881
Tigridia sp.	+	–	Mangiferin, 1 Dk absorbing negatively charged compound	K	312–83.03822
Tigridia sp.	+	–	Mangiferin	K	441–75.04555
Tigridia sp.	+	–	Mangiferin	K	312–83.0384
Tigridia sp.	+	–	Mangiferin, Isomangiferin	K	312–83.03840
Tigridia sp.	+	–	ProCy, ProDp	K	312–83.03544
Tigridia sp.	+	–	ProCy	K	312–83.08543
Trimezieae					
Neomarica caerulea (Ker-Gawl.) T. Sprague	+	–	ProCy 2 Dk/Dk unident.	K	423–78.06355
N. gracilis (Herb. ex Hook.) T. Sprague	+‡	–	ProCy, ProDp	K	393–75.066283
N. northiana (Schneev.) T. Sprague	+‡	–	ProCy, ProDp 2B-negatively charged compounds	M	
	+‡	–	ProCy, ProDp	K	301–79.06117
Trimezia juncifolia (Klatt) Benth. & Hook. f.	+	–	–	MO	Irwin, Souza & Reis dos Santos 11810
T. martii (Baker) R. Foster	+‡	–	–	M	
	+‡	–	–	K	400–76.03900
	+‡	–	ProCy, ProDp	K	301–79.02650
	+‡	–	ProCy	K	301–79.06027
T. martinicensis (Jacq.) Herb.	+‡	–	–	K	ARM S. May 191
	+‡	–	–	K	131–74.07210
T. rupestris Ravenna	+	–	ProCy, ProDp	MO	Irwin, Harley & Onishi 29115
T. steyermarkii R. Foster	+	–	Ap *C*-glyc *O*-glyc SO_4	MO	T. B. Croat 40408
	(+)	–	Dk/Dk unknown Ap *C*-glyc *O*-glyc SO_4 ProCy, ProDp, ProPg	MO	Peter Goldblatt

Ixioideae					
Watsonieae					
Lapeirousia corymbosa subsp. *fastigiata* (Lam.) Goldbl.	–	Qu, Km, Isorh.	–	MO	P. Goldblatt 5852
L. fabricii (de la Roche) Ker	–	My, Qu, Km	Mangiferin, Mangiferin *O*-RG	MO	P. Goldblatt 6714
L. rhodesiana N. E. Br.	–	My, Qu, Km	–	K§	Mrs. H. M. Richards 10957
Pillansia templemannii L. Bolus	–	Qu, Isorh, My	Isorh 3-SO_4	SAM	Williams 3596
Watsonia humilis Miller	–	Qu, Isorh	–	K	306–83.03488
W. pyramidata (Andr.) Stapf.	–	My, Qu	ProDp	R	840140
Ixieae					
Anomalesia splendens (Sweet) N. E. Br.	+	–	Tricin	M	
Anomatheca laxa (Thunb.) Goldblatt	–	Km	–	K	356–63.35603
	–	Qu, Km	–	R	800438
	–	–	Fluorescent Y unident.	R	
A. verrucosa (Vogel) Goldblatt	–	(Qu) Km	–	R	840138
Antholyza ringens L.	–	Qu	–	M	
Babiana patula N. E. Br.	+	My	–	K	110–82.00926
B. stricta (Ait.) Ker.-Gawl.	–	My, Qu	ProDp	R	730050
Babiana sp.	–	My	ProCy, ProDp	K	046–83.00383
Chasmanthe bicolor (Gasp.) N. E. Br.	–	My, Qu, Km	ProDp	R	801029
Crocosmia cv. 'solfataire'	–	My, Qu	ProCy	S	
Crocosmia × *crocosmiflora* (Lemoine) N. E. Br.	–	My, Qu	ProCy	S	
Crocus aureus Sibth. & Sm.	(+)	–	Mangiferin	–	Hort. source unknown
C. cancellatus Herbert	+	Qu	Dk/Y unident.	R	771076
C. chrysanthus Herbert cv. 'Cream Beauty'	(+)	–	6OH Lu 7-Glc, Scut 7-Glc	–	Obtained commercially
C. corsicus Maw	+	–	6OHLu7ME 6Glc, Scut 7ME 6Glc	–	Obtained commercially
Crocus etruscus Parl	–	Km (3-soph)	–	–	Hort. source unknown
C. fleischeri Gay	–	–	–	–	Obtained commercially
C. goulimyi Turrill	+	–	–	K	Hort. origin Cytology No. 691125
C. heuffelianus Herbert	+	–	Tricin	K	Cytology No. 701446
C. korolkowii Maw & Regel	+	Qu, Km	–	K	PF6208 Cytology No. 70154
C. laevigatus Bory & Chaub	–	Km, (3-soph)	Aca	–	Hort. origin, source unknown
C. minimus DC.	+	–	6OHLu 7RG, 6OHLu 7ME 7RG, Scut 7ME 6Glc, Ap	–	Obtained commercially

Table 1. (*Continued*)

Subfamily* tribe, species	Flavone C-glycosides	Flavonols	Others	Plant source†	Accession number or collectors name or number
C. niveus Bowles	+	–	–	K	641–86.00155
C. sativus L.	+	Km	–	Km	Iraq Cytology No. 691368
C. sieberi Gay	+	Km	–	Km	Greece Cytology No. 691357
C. tommasinianus Herbert cv. 'Whitewell Purple'	+	–	Tricin, Ap 4 Dk/Y negatively charged compounds	R	751313
Crocus tournefortei Gay	+	–	–	R	771092
C. vernus Hill	+	–	–	K	Sicily Cytology No. 701507
C. vernus Hill var. *albiflorus*	+	Km	–	K	Yugoslavia Cytology No. 71159
C. versicolor Ker-Gawl.	–	Km (3-soph)	–	–	Hort. source unknown
Dierama pulcherrimum (Hooker fil.) Baker	–	Qu, Km, Isorh, My	–	R	
Freesia alba (G. L. Meyer) Gumbleton	+	–	–	K	306–83.03489
F. refracta (Jacq.) Klatt	+	–	–	M	
F. sparrmannii N. E. Brown	–	Km	–	K	306–83.03486
Gladiolus byzantinus Mill.	–	Qu, Km, Isorh	–	–	obtained commercially
G. carmineus C. H. Wright	–	–	Lu, Ap	K	165–65.16502
G. delenii Van-Geel	–	Qu, Km	–	K	287–77.02187
G. floribundus Hort.	+	Km	Tricin as 5 glycoside? 2C/B negatively charged compounds	M	Montagu, S. Africa
G. illyricus Koch	–	Qu, Isorh, Km	–	R	73002
G. illyricus Koch	–	Isorh	Dk/Y unident.	K	000–72.10302
G. italicus Mill.	–	–	Lu, Ap	K	326–79.02990
G. papilio Hook. f.	+	–	Tricin, Ap, Lu, ProDp, Dk/Dk unident.	R	840413
G. scullyi Baker	–	Qu, Km	Tricin, Lu, ProCy	K	110–82.00931
G. segetum Ker-Gawl.	–	Isorh	Dk/Y unident. (as in *G. illyricus*)	K	000–69.13732
G. tristis L. var. *concolor*	+	Qu, Isorh	Lu, Tricin (as 5-Glucosides) 2 Dk/Dk unident.	R	681590
G. triphyllus Bertol.	+	–	Tricin	K	162–81.02201
Hesperantha falcata (L.f.) Ker-Gawl.	+‡	—	–	K	306–83.03480
H. muirii (L. Bolus) Lewis	+	–	–	D	
Homoglossum priori (N. E. Brown) N. E. Brown	+‡	—	–	M	
Ixia rapunculoides Delile	–	Qu, My	ProCy, ProDp negatively charged C/B compound	M	
Melasphaerula graminea Ker-Gawl.	–	Qu, Km	Dk/Dk negatively charged compound	M	
Oenostachys abyssinica (A. Brongn.) N. E. Br.	–	Qu	Ap	M	
Romulea bulbocodium (L.) Sebastian & Mauri	–	Qu, Km, Isorh	–	R	730574

R. dichotoma Baker	–	Qu	–	K	312–77.02406
R. elliptica de Vos	–	Qu, Km	–	M	M. P. De Vos 2017
R. hirta Schlr.	+	–	–	K	312–77.02407
R. nivalis Boss et Ky	–	Qu, Km, Isorh	–	R	790423
R. sabulosa Schlr.	–	Qu, My	Tricin	K	326–79.02965
R. saldanhensis de Vos	–	Km	–	K	259–77.02004
Schizostylis coccinea Backh. & Harv.	+	(Qu)	–	K	no accession no.
Sparaxis grandiflora (de la Roche) Ker-Gawl.	–	(Qu)	–	RNG	J. E. Lousley 881
S. tricolor (Schneev) Ker-Gawl.	–	Qu, Km, My	Plumbagin	K	312–77.06928
Synnotia villosa (Burm. f.) N. E. Brown	–	Qu, Km	2 Dk/Dk negatively charged compounds	K	236–77.01863
Tritonia dubia Eckl.	–	Qu, Isorh, My	–	M	
T. crocata (L.) Ker	–	Qu, Km, My	–	K	306–83.03487

*Classification according to P. Goldblatt [4, 5 and unpublished work] and *Iris* according to Mathew [42].

†Plant sources: D = plant material from the private garden of Dr. M. W. Dick, Botany Department, University of Reading; H = plant material from the private garden of Mr. D. J. N. Hind of the Royal Botanic Gardens, Kew; K = plants from the living collection, The Royal Botanic Gardens, Kew; M = material supplied by Brian Mathew of the Royal Botanic Gardens, Kew; MO = material received from Dr. Peter Goldblatt, Missouri Botanic Garden; NSW = National Herbarium of New South Wales; R = plants growing at the Plant Science Laboratories, University of Reading; RNG = The Herbarium, Plant Science Laboratories, University of Reading; S = plant material from the private garden of Mrs. R. M. Souster of Goring-on-Thames and SAM = plant material from the South African Museum Herbarium, Kirstenbosch.

Key: Qu = quercetin; Km = kaempferol; My = myricetin; Isorh = isorhamnetin; Lu = luteolin; Ap = apigenin; Aca = acacetin; 60H Lu 7ME = 6-hydroxyluteolin 7 methyl ether; Scut 7ME = scutellarein 7-methyl ether; Glc = glucoside; RG = rutinoside; Dk/Dk = dark in UV light plus ammonia; Dk/Y = dark to yellow in UV light plus ammonia; B = blue in UV light; C/B = colourless to blue in UV light plus ammonia; ProCy = procyanidin; ProDp = prodelphinidin; ProPg = propelargonidin; ( ) = trace constituent.

‡Methylated derivatives are present in this species.

||Another orange to yellow (in UV + NH_3) constituent (R_f BAW 19 and 15% HOAc 63) also present.

§Another two orange to yellow (in UV + NH_3) constituents (R_fs BAW 06, 06 and 15% HOAc, 26, 53) also present.

Table 2. Flavonoid glycosides identified in the leaves of some Iridaceae species

Tribe, species	Flavonoid glycosides identified
Aristeae	
Klattia partita	My 3-glucoside and 3-galactoside, My 3-arabinosylgalactoside*, My 3-rhamnosylarabinosylgalactoside* and 3-rhamnosylarabinosylglucoside*, Qu 3-glucoside and 3-galactoside, Qu 3-rhamnosylarabinosylgalactoside*, Isorh 3-glucoside and 3-galactoside, Km 3-rhamnosylarabinosylgalactoside* and 3-rhamnosylgalactosylglucoside*
K. stokoei	My 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside. My 3-rhamnosylglucoside, 3-rhamnosylgalactoside and 3-galactosylglucoside* Qu 3-α-L-arabinopyranoside, Qu 3-rhamnoside, Qu 3-diglucoside, 3-digalactoside and/or 3-galactosylglucoside*, Km 3-rhamnosylarabinoside*, 3-rhamnosylglucoside* and/or 3-arabinosylglucoside*
Nivenia fruticosa	Qu 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside, Qu 3-galactosylglucoside* acylated ? (two compounds with different R_fs) Isorh 3-glucoside and 3-galactoside Km 3-glucoside Km 3-galactosylglucosides* acylated? (two compounds with different R_fs)
N. stokoei	My 3-rhamnoside, Qu 3-galactoside, 3-arabinoside and 3-rhamnoside, Qu 3-rhamnosylarabinosylglucoside* and two Qu 3-rhamnosylgalactosylglucosides*
Patersonia fragilis	Qu 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnosylglucoside* acylated? Isorh 3-glucoside, 3-galactoside and 3-arabinoside, two Isorh 3-rhamnosylglucosides* acylated?
P. glabrata (R. Coveny 11834)	Amentoflavone, Or, IsoOr, Vit, Lu di-C-glycoside
P. longifolia	My 3-glucoside, 3-galactoside and 3-rhamnoside
P. sericea	My 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside My 3-rhamnosylglucoside and 3-rhamnosylgalactoside Qu 3-rhamnoside Isorh 3-glucoside, 3-galactoside, 3-arabinoside and 3-rhamnoside 2 unidentified DK/DK aglycones
Witsenia maura	My 3-arabinoside, 3-rhamnosylglucoside and rhamnosylgalactoside Qu 3-α-L-arabinopyranoside, Isorh 3-glucoside, 3-galactoside, 3-arabinoside, 3-rhamnosylglucoside and 3-rhamnosylgalactoside, Isorh 3-diglucoside, 3-digalactoside and/or 3-galactosylglucoside*
Irideae	
Moraea bellendenii	Tricin 5-glucoside and two tricin 7-glucosides
Watsonieae	
Pillansia templemannii	My 3-glucoside, 3-galactoside, 3-arabinoside, 3-rhamnoside, 3-diglucoside and 3-rhamnosylglucoside Qu 3-galactoside and 3-rhamnoside Isorh 3-SO_4 and 3-galactoside
Ixieae	
Crocus chrysanthus cv. Cream Beauty	6-OHLu 7-glucoside Scut 7-glucoside
C. corsicus	6-OHLu 7-ME 6-glucoside Scut 7 ME 6-glucoside
C. minimus	6-OHLu 7-rutinoside 6-OHLu 7 ME 6-glucoside Scut 7 ME 6-glucoside
C. tommasinianus	Or and IsoOr *O*-glucosides Vit and Isovit *O*-glucosides Tr diglucoside Ap *O*-glucoside Free Tr
Gladiolus tristis	Qu 3-glucoside Lu and Tr 5-glucosides Lu and Tr glucosides with high R_f in H_2O (45) Tr-diglucoside IsoOr 7-rhamnosylglucoside* IsoOr 7-rhamnosylarabinosylglucoside*

*The order of sugars in these compounds was not determined.

Key: My = myricetin, Qu = quercetin, Isorh = isorhamnetin, Km = kaempferol, Lu = luteolin, Ap = apigenin, Tr = tricin, Or = orientin, IsoOr = iso-orientin, Vit = vitexin, 6-OHLu = 6-hydroxyluteolin, Scut = scutellarein, ME = methyl ether, DK/DK = dark to dark in UV light plus NH_3.

hydrolysis and flavonoid sulphates detected by paper electrophoresis at pH 2.2. Both the xanthone mangiferin and the naphthoquinone plumbagin were isolated from methanolic leaf extracts and identified by comparison with authentic markers. Biflavonoids were detected by their appearance as dark to dark compounds in UV light plus ammonia and their position, high in BAW and just mobile in 15% acetic acid, on a two dimensional paper chromatogram. They were purified by PC in BAW followed by preparative TLC (see Experimental). They were characterized by their UV spectra, R_f comparison with authentic markers and, when possible, by FAB-MS.

The flavone *C*-glycosides present were assumed to be generally of the normal type, i.e. derivatives of vitexin, isovitexin, orientin or iso-orientin, from their behaviour on 2D chromatograms when compared with these standards. Additionally, in leaves of about 40 species, glycoflavones were found with the typical mobilities of methylated derivatives and these species are so indicated in Table 1. Glycoflavones based on apigenin 7-methyl ether, the 4'-methyl ether or the 7,4'-dimethyl ether have already been reported in the family, mainly from *Iris* [12, 13] but also from *Fosteria*, *Rigidella* and *Sessilanthera* [16] and it is likely that these compounds we have now detected are of a similar type.

Flavone *C*-glycosides and flavonols were found to be the most frequent leaf constituents in the Iridaceae (Table 1), present in 66% and 32% of species, respectively. The distribution of some rarer phenolics, namely mangiferin (in 17% of the sample), the quinone plumbagin (in 4%), the biflavonoid amentoflavone in *Patersonia glabrata* [15] and 6-hydroxyflavones in three *Crocus*

species [14] have been previously reported but some additional findings are given here (see Table 1).

The results are probably best considered at subfamily and tribal levels (Table 3). Thus, the subfamily Isophysidoideae with its single species, *Isophysis tasmanica*, is characterized by the presence of three biflavonoids: amentoflavone, 2,3-dihydroamentoflavone and what is probably sotetsuflavone (amentoflavone 7′-monomethyl ether) as major leaf constituents and only trace amounts of glycoflavones. This is the first report of 2,3-dihydroamentoflavone in the Iridaceae and in the monocotyledons.

In contrast, flavone *C*-glycosides are the main leaf flavonoid components in four of the five tribes of the subfamily Iridoideae: in the Irideae, Sisyrinchieae, Tigrideae and Trimezieae. However, the Irideae and Tigrideae may be distinguished by the frequent occurrence of the *C*-glucosylxanthone mangiferin and the Trimezieae and Sisyrinchieae by the absence of flavonols. Within the Irideae mangiferin was previously shown [8, 9, 15, 17, 18] to be characteristic of *Iris* species of subgenus *Iris* section *Iris*, subgenus *Limniris* series *Laevigata* and *Unguicularis* and in the three *Gynandriris* species surveyed. It was also found in *I. flavissima* Pallas (section *Psammiris*) [8] and *I. setosa* (section *Iris* subgenus *Limniris* series *Tripetalae* [17]. We now report mangiferin, often accompanied by its isomer isomangiferin, and sometimes an *O*-glycoside from all the species examined in subgenus *Iris*, including 15 taxa from section *Iris*, *I. humilis* from section *Psammiris* and *I. hoogiana* from section *Regelia*. Amongst species of the subgenus *Limniris* section *Limniris* mangiferin was found as a major constituent in members of four of the ten series surveyed: in the *Tripetalae*, *Laevigatae*, *Ensatae* and *Unguiculares*. It was also identified in the two taxa examined from subgenus *Hermodactyloides*. Flavone *C*-glycosides were detected in all but two of the 58 *Iris* species surveyed but flavonols were found in only nine taxa, all except one in subgenus *Limniris*.

In the Tigrideae mangiferin was detected by us in some *Eleutherine*, *Gelasine*, *Rigidella* and *Tigridia* species but was absent from the other four genera surveyed [15]. We have since found it also in *Ennealophus boliviensis*. Ballard and Cruden [16] have also reported mangiferin to be present in the Tigrideae, in leaves of four *Rigidella* species, and of one *Sessilanthera* and one *Fosteria* species. However, in some taxa of *Calydorea*, *Cipura*, *Cypella* and in *Tigridia pavonia* (which do not synthesize mangiferin) and in two *Eleutherine* species and in *Gelasine azurea* (which do) dark to dark and/or dark to yellow (in UV $+NH_3$) negatively charged compounds were detected, which are possibly flavonoid sulphates. These constituents were otherwise only found in one *Iris* species, in one *Trimezia* species (Trimezieae) and in a few members of the Ixioideae. In *Trimezia steyermarkii* an apigenin *C*-glycoside-*O*-glucosidesulphate was partially characterized.

Luteolin, apigenin and tricin *O*-glycosides occurred occasionally in all the tribes of the Iridoideae except the Trimezieae and tricin was sometimes present in the free state, e.g. in one specimen of *Patersonia glabrata* (P. Hind 3557). In the Sisyrincheae it is of some taxonomic interest that *Phaiophleps biflorus* subsp. *biflorus* should exceptionally produce only luteolin glycosides and some free luteolin, whereas in *P. biflorus* subsp. *lyckholmii*, which was once treated as a separate species [19], flavone *C*-glycosides were the main constituents and luteolin was not detected. Another *Phaiophleps* species, *P. acaule*, was distinguished by the presence of the quinone plumbagin, previously found in the Sisyrinchieae only in two *Sisyrinchium* species [15].

The Aristeae, by contrast, was chemically very different from all the other tribes of the Iridoideae in the predominance of flavonol glycosides and the occurrence of the quinone, plumbagin. The flavonoids of nine members of the Aristeae were therefore examined in more detail (see Table 2). In these plants myricetin and isorhamnetin glycosides were most frequent but quercetin and kaempferol derivatives were also present. Four of the taxa examined: *Klattia partita*, *K. stokoei*, *Nivenia fruticosa* and *Witsenia maura*, all from South Africa, contained complex mixtures of flavonol monoglycosides, i.e. the 3-arabinosides, 3-glucosides, 3-galactosides and 3-rhamnosides of myricetin, isorhamnetin, quercetin and kaempferol together with unusual di- and/or triglycosides of these aglycones. In the triglycosides three different sugars were detected all attached at the 3-position, e.g. quercetin 3-(rhamnosylarabinosylglucoside) and two 3-(rhamnosylgalactosylglucosides) in *Nivenia stokoei*. Unfortunately there was not sufficient plant material to determine the order of the sugars although FAB-MS was tried on some of the compounds. The myricetin triglycosides were particularly labile, which added to the difficulties. Of the remaining genera of the Aristeae *Aristea* is clearly distinguished by the presence of plumbagin in all seven species examined. Quercetin and kaempferol were also more common in these taxa, myricetin absent and isorhamnetin rare.

Six species of the Australian genus *Patersonia* were previously analysed [15]. Flavonol glycosides were again the main constituents in all species except four of the five samples of *P. glabrata*. However, only mono- and diglycosides were found although there was some evidence of acylation in *P. fragilis*. Myricetin and isorhamnetin were once more the most common aglycones with some quercetin but no kaempferol derivatives identified. The sugars were similar to those found in other members of the Aristeae: namely galactose, glucose, arabinose and rhamnose. The other three samples of *P. glabrata* were different from all the other taxa of the Aristeae surveyed in the presence of glycoflavones and the biflavonoid, amentoflavone, as the major leaf components [15]. However, some unidentified dark to dark (in UV + NH_3) aglycones in *P. sericea*, *P. occidentalis*, *Klattia partita*, *Nivenia stokoei* and *Witsenia maura* from their R_fs and UV spectral data may also be biflavonoids although they did not co-chromatograph with any of the readily available amentoflavone methyl ethers. In fact the spectra of some suggest they may be luteolin derivatives. As yet unidentified aglycones with similar R_f, colour and spectral properties were also isolated from four *Moraea* species in the Irideae, a *Cypella* species in the Tigrideae and one sample of *Trimezia steyermarkii* in the Trimezieae.

The remaining subfamily, the Ixioideae, has only two tribes: the Watsonieae and the Ixieae. All six members of the Watsonieae that were examined gave similar flavonol profiles with no flavones or glycoflavones. One of them, *Lapeirousia fabricii*, additionally produced mangiferin. Quercetin was universally present with myricetin in four taxa and isorhamnetin and kaempferol in three species each. However, the South African taxon *Pillansia templemannii* was unique in the tribe Ixioideae (and in the

Table 3. The percentage occurrence of leaf flavonoids and other phenolics in tribes of the Iridaceae

Subfamily tribe*	No. of species surveyed†	Pro Cy	Flavone C-glycosides	Flavones					Flavonols						
				Lu	Ap	Tr	Aca	6-OH flavones	Km	Qu	My	Isorh	Mang	Plumbagin	Biflavones
Isophysidoideae	1	—	100 (trace only)	—	—	—	—	—	—	—	—	—	—	—	100
Iridoideae															
Aristeae	19	39	5	—	—	5	—	—	59	95	39	53	—	39	32‡
Irideae	88	11	82	1	—	1	—	—	5	15	8	1	33	—	6§
Sisyrinchieae	37	11	97	5	3	—	—	—	—	—	—	—	—	8	11§
Tigrideae	26	19	100	—	—	4	—	—	4	—	—	4	50	—	4§
Trimezieae	8	63	100	—	—	—	—	—	—	—	—	—	—	—	—
Ixioideae															
Watsonieae	6	17	—	—	—	—	—	—	50	100	67	50	17	—	—
Ixieae	62	11	44	8	10	15	2	5	40	47	19	15	2	2	—

*Classification according to Goldblatt [4, 5 and unpublished work].

†Includes subspecies but not varieties.

‡One of these compounds was identified as amentoflavone but constituents from five other species with similar R_f, UV colour reactions and spectral data were not fully characterized.

§These compounds were not fully characterized but had similar R_f, colour and UV spectral properties to biflavonoids.

Key: ProCy = proanthocyanidins, Lu = luteolin, Ap = apigenin, Tr = tricin, Aca = acacetin, 6-OH = 6-hydroxy, Km = kaempferol, Qu = quercetin, My = myricetin, Isorh = isorhamnetin, Mang = mangiferin.

Iridaceae) in producing a flavonol sulphate. Isorhamnetin 3-sulphate was characterized as a major leaf constituent in this plant together with several mono- and diglycosides of myricetin, quercetin and isorhamnetin and two unidentified triglycosides of quercetin and isorhamnetin similar to those found in some South African members of the Aristeae. The Ixieae differ from all the other tribes of the Iridaceae in the great diversity of flavonoids and other phenolics present. In this tribe not only were glycoflavones and flavonols both frequent (in 44% and 68% of species, respectively) but they often occurred together. Myricetin was detected in species of six genera (19% of the sample) but quercetin was the most common flavonol (present in 47% of taxa) with kaempferol (in 40%) and isorhamnetin (in 15%) also well represented. A number of flavones: luteolin, apigenin, tricin and acacetin and some more unusual 6-hydroxylated derivatives were also detected in the Ixieae. Most of these compounds were found in *Crocus* and *Gladiolus* species, although tricin was also identified in *Anomalesia splendens* and *Romulea sabulosa*. In a previous communication [14] we reported the characterization of 6-hydroxyluteolin 7-glucoside and 7-rutinoside, 6-hydroxyluteolin 7-methyl ether 6-glucoside, scutellarein 7-glucoside and scutellarein 7-methyl ether 6-glucoside in three *Crocus* species (see Table 2). We now report a number of flavone *C*- and *O*-glycosides and free tricin from *Crocus tommasinianus* and luteolin and tricin 5-glucosides, quercetin 3-glucoside and two highly glycosylated iso-orientin derivatives from *Gladiolus tristis*. All the *Gladiolus* species examined gave very complex flavonoid profiles and warrant further study. A number of different patterns were found: (1) flavonols alone, (2) flavones alone, (3) flavonols plus flavones, (4) flavone *C*-glycosides plus flavones and (5) flavones, flavonols and glycoflavones. Other unusual constituents found in the Ixieae include mangiferin in *Crocus aureus* and plumbagin in *Sparaxis tricolor*.

Proanthocyanidins occur sporadically as leaf constituents throughout the Iridaceae, although they are most frequent in the Trimezieae (in 63% of species) and the Aristeae (in 39% of taxa). They co-occur with either flavone *C*-glycosides or flavonols. Procyanidin was found most frequently. Apart from one exceptional *Nivenia* species, prodelphinidin was only detected in those taxa that also synthesized myricetin. Propelargonidin was once detected in the family, in *Trimezia steyermarkii*.

Floral constituents

In general, it has been difficult to combine a survey of leaf constituents with a similar survey of floral tissue, because of the limited availability of fresh flowers. There is little available in the literature on floral flavonoids, apart from studies of *Iris* [11, 20] and our own earlier report on *Crocus* [14]. Here we report briefly on the anthocyanins of four species and on the flavonol glycosides of two others.

Earlier work on the anthocyanins of Iridaceae petals is summarized in ref. [11]. The only major more recent study seems to be the investigation of the cultivated *Gladiolus*, where the 3-rutinosides, 3-rutinoside-5-glucosides and 3,5-diglucosides of the six common anthocyanidins have been variously identified in different colour forms [21]. We now report the identification of cyanidin 3-glucoside in the scarlet flowers of *Schizostylis coccinea*, and of cyanidin 3-rutinoside in the red petals of *Anomatheca laxa*. Two more unusual pigments, the 3-diglucosylrhamnoside and 3-rutinoside of petunidin were found in the deep blue corollas of a *Sisyrinchium* species currently being investigated at Reading by Professor D. M. Moore. Finally, an acylated delphinidin 3-diglucoside was detected in *Lapeirousia corymbosa* but lack of material prevented its full characterization. This is the only pigment in the family of some 20 species surveyed to be zwitterionic, but the nature of the aliphatic acylating acid is not yet known.

As will be seen (Table 4), a number of different glycosidic patterns are present in the anthocyanins of this

Table 4. Anthocyanin pigments identified in floral tissues of the Iridaceae

Genus and species	Pigments identified*
IRIDOIDEAE	
Iris spp.	Dp and Mv 3-(*p*-coumaroylrutinoside)-5-glucosides
Sisyrinchium sp.	Pt 3-diglucosylrhamnoside† and Pt 3-rutinoside†
IXIODEAE	
Anomatheca laxa	Cy 3-rutinoside†
A. verrucosa	Cy 3-rutinoside
Babiana stricta	Mv 3,5-diglucoside
Chasmanthe ethiopica	Cy and Pn 3-rutinosides
Crocosmia masonii	Cy 3,5-diglucoside and Cy 3-rutinoside-5-glucoside
Crocus spp.	Dp 3,5-diglucoside
Freesia cv.	Mv 3-glucoside
Gladiolus gandavensis	Pg, Cy, Dp, Pn, Pt and Mv 3-rutinosides, 3-rutinoside-5-glucosides and 3,5-diglucosides
Lapeirousia corymbosa	Dp 3-diglucoside†‡
Schizostylis coccinea	Cy 3-glucoside†
Tritonia cv. Prince of Orange	Pg 3-gentiobioside
Watsonia meriana, *W. rosea* and *W. tabularis*	Pg 3-glucoside, Pg 3-sophoroside and Pg 3-sophoroside-7-glucoside

*Most reports from Harborne [11], for *Gladiolus* see ref. [21].

†Newly reported.

‡This pigment is acylated with an aliphatic organic acid, but other anthocyanins in Iridaceae are not zwitterionic [see Harborne, J. B., unpublished results].

family. The subfamily Iridoideae would seem to be characterized by the presence of hydroxycinnamic acid acylation (widespread in *Iris*) and of 3-rutinoside substitution. By contrast, the members of the Ixioideae are more diverse, with rutinoside, sophoroside and gentiobioside having been variously recorded. However, wider surveys are still needed to confirm that there are differences in anthocyanin synthesis at the subfamily level.

It is likely that there are also differences in floral flavones and flavonols between these two subfamilies, since glycosylflavones have been found in the Iridoideae and flavonol glycosides in the Ixioideae. Unpublished results on the flowers of 15 *Iris* species and of various cultivars has indicated the presence in all cases of major amounts of *C*-glycosylflavones and the concurrent absence of flavonol glycosides. This is supported by the literature reports of particular glycosylflavones having been identified in flowers of *Iris germanica*, *I. japonica* and *I. nertshinskia* var. *alba* [12, 13]. By contrast, there are no reports so far of glycosylflavones in flowers of the Ixioideae, but flavonol glycosides have been found.

Thus, in flowers of ten *Crocus* species, kaempferol glycosides were recorded as major constituents [14]. Present examination of flowers of *Gladiolus tristis* and *Lapeirousia corymbosa* confirm this trend within the Ixioideae. Thus *G. tristis* yielded five flavonol glycosides, the 3-galactosides of kaempferol, quercetin, myricetin, larycitrin (myricetin 3′-methyl ether) and syringetin (myricetin 3′,5′-dimethyl ether). This identification of larycitrin and syringetin is of some general interest in as much as this is the first record of these two methyl ethers in the Iridaceae. Both have, however, been reported in relatively rare instances in other monocot families, notably the Zingiberaceae [22] and the Restionaceae [23]. Similar analysis of flowers of *Lapeirousia corymbosa* showed the presence of 3-glucosides, 3-galactosides and 3-arabinosides of kaempferol and of quercetin. Such a glycosidic pattern is a common one among the flavonols present in the leaves of related species (see Table 2).

DISCUSSION

The summary of the present data at subfamily and tribal levels (Table 3) clearly displays the great diversity of flavonoid and other phenolic structures found within the Iridaceae. All the main classes of flavonoids are represented, although glycoflavones and flavonols are the characteristic leaf constituents in the family. The three subfamilies appear to be both morphologically and chemically well defined. But the discovery of biflavonoids as major components in *Isophysis tasmanica* (Isophysidoideae) is particularly significant as it lends good support to the suggestion that this is a relic plant of ancient origin. Its floral structure and leaf form has led Goldblatt [24] to postulate that the ancestral Iridaceae resembled *Isophysis*. Biflavonoids, although characteristic constituents of the gymnosperms, are found only occasionally in the dicots and very rarely in monocots. We recently reported amentoflavone from *Patersonia glabrata* [15] but previously there was only one other mention of a biflavonoid, namely of a 3,8-linked biflavanone, from stems of *Lophiola americana* Wood (Melanthiaceae [3]) [25]. Our findings in *Isophysis* therefore represent the second report of amentoflavone and the first record of 2,3-dihydroamentoflavone in the Iridaceae and the monocotyledons.

The Iridoideae are a large assemblage of plants with five chemically easily distinguished tribes. The phenolic results support Goldblatt's latest arrangement [4, 5 and unpublished work] of this subfamily showing a trend from the flavonol-rich Aristeae, through the Irideae with increasing frequence of flavone *C*-glycosides and the corresponding decrease in flavonol constituents to the glycoflavone-based tribes Sisyrinchieae, Tigrideae and Trimezieae. However, the major complex of genera which form the tribe Irideae has radiated in the Old World, while the latter two tribes are probably more recent and have developed almost entirely in the New World. The Sisyrinchieae is distributed in both America and Australia whilst the Aristeae is largely of South African origin with the exception of the Australian genus, *Patersonia*. A number of the phenolic characters represented in the Aristeae, for example, biflavones, plumbagin, myricetin and flavone *C*-glycosides could be regarded as 'primitive' markers. Thus, the occurrence of biflavones, myricetin and glycoflavones in the genus *Patersonia* would suggest that this is a primitive group within the Iridaceae. Also the finding of amentoflavone in both *Isophysis* and *Patersonia* and the possibility of the presence of biflavonoids in other members of the Aristeae forms a chemical link between this tribe and the Isophysidoideae thus confirming the basal nature of the former in the Iridoideae. Similarly, the presence of the naphthoquinone, plumbagin, in all members of the South African genus *Aristea* supports this arrangement since this genus is regarded as unspecialized both florally and in its unmodified storage organs. Quinones were otherwise found only in three species of the Sisyrincheae and in *Sparaxis tricolor* (Ixieae). Biflavonoids on the other hand are possibly present in the Irideae and Tigrideae.

Another unusual phenolic, the *C*-glucosylxanthone mangiferin does not apparently have any phyletic significance within the family but is of systematic interest in its linking of the Tigrideae with the Irideae. Thus, within the Tigrideae it was identified in *Eleutherine*, *Ennealophus*, *Gelasine*, *Rigidella* and some *Tigridia* taxa but was not found in *Calydorea*, *Cipura*, *Sphenostigma* and *Herbertia*. This distribution pattern unfortunately does not entirely agree with Goldblatt's recent treatment of the tribe based on chromosome number [26]. However, the absence of mangiferin and the presence of possible flavonoid sulphates in *Tigridia pavonia* does distinguish this plant from the other *Tigridia* species surveyed, from which it is also morphologically distinct. Within the Irideae mangiferin forms a good chemical marker for a number of *Iris* groups as already mentioned above.

The present evidence also supports the removal of the genus *Bobartia* from the Sisyrinchieae/Aristeae to the Irideae, where it fits in better both anatomically [27] and chemically. Similarly, the predominance of glycoflavones in *Diplarrhena*, another genus of uncertain affinity suggests that it should be placed in the Irideae near to *Dietes*. Also the two subspecies of *Phaiophleps biflorus*, subspecies *biflorus* and *lyckholmii*, are sufficiently distinguished by their leaf flavonoid profiles to suggest that the latter should once more be treated as the separate species, *P. lyckholmii*, in agreement with recent morphological evidence [19].

The subfamily Ixioideae is distinguished in having the widest range of phenolic constituents with glycoflavones, flavonols and flavones all being well represented. Two of the most morphologically specialized genera *Crocus* and

Table 5. A comparison of the leaf flavonoids of the Iridaceae with those of some other monocot groups

Order or family	Flavone C-glycosides	Flavonols	Flavones (Lu, Ap, Aca or Chrys)	Proantho-cyanidins	Tricin	6-Hydroxy-flavonoids	Flavonoid sulphates	Mangi-ferin	Biflavo-noids	Quinones	Ref-erences
Araceae	+++	++	(+)	++	–	–	(+)	–	–	–	[31]
Amaryllidaceae	–	+++	–	(+)	–	–	–	–	–*	–	[32]
Bromeliaceae	+	++	+	–	–	+	–	–	–	–	[33]
Commelinaceae	+++	++	(+)	nd	(+)	+	(+)	–	–	–	[34]
Cyperaceae	++	+	++	++	+++	(+)	+	(+)	–	–	[2]
Fluviales	++	(+)	+	(+)	–	–	+	–	–	–	[35]
Gramineae	+++	(+)	+	(+)	+++	–	+	–	–	(+)	[36]
Iridaceae	+++	++	(+)	+	(+)	(+)	(+)	+	(+)	(+)	—
Juncaceae	(+)	(+)	+++	+	–	–	+	–	–	–	[37]
Liliaceae	(+)	+	++	+	(+)	–	(+)	(+)	–	(+)	[32]
Orchidaceae	++	++	(+)	(+)	(+)	+	(+)	–	–	–	[38]
Restionaceae	+	+++	+	+++	–	+†	(+)	–	–	–	[21, 39]
Palmae	+++	+	+	+++	++	–	+++	–	–	–	[40]
Zingiberales	+	++	+	+++	–	–	(+)	–	–	–	[20]

(+)In < 10% of species; + in 10–25% of species; ++ in 25–50% of species; +++ in > 50% of species; nd = not determined.

*A 3,8-linked biflavanone has been reported from the stems of *Lophiola americana* [25].

†8-Hydroxylation in the case of Restionaceae.

Gladiolus also show the greatest chemical complexity. The presence of 6-hydroxylated flavones in *Crocus* is of particular significance since these compounds are generally regarded as being chemically 'advanced'.

In most modern classification systems [e.g. 28–30] the Iridaceae are placed in the same order as the Liliaceae and Amaryllidaceae and a comparison of the present data with that of these and some other monocot families previously screened (Table 5) indicates that there are some chemical links. But it is also clear that the Iridaceae can be chemically distinguished from these and the other monocot families in the diversity of its phenolic profile and the presence of several otherwise rare constituents, especially biflavonoids, quinones and mangiferin. The present discovery of plumbagin in four genera extends the number and type of quinone pigments isolated from the family [15].

Lastly, the finding of biflavonoids in the Iridaceae may reflect the persistence of an ancient feature of the primitive tribes of the family and suggests considerable antiquity for the Iridaceae. The family is undoubtedly specialized in many ways but may have diverged very early from the basal stock of the monocotyledons.

Table 6. R_f (× 100) data for some partially characterized flavonoid di- and triglycosides found in the Iridaceae*

Flavonoid	Solvents BAW	15% HOAc	H_2O	CAW (1:1)
Myricetin				
3-glucoside†	28	14	03	16
3-rhamnosylglucoside‡	48	35	14	17
3-arabinosylgalactoside†	25	52	17	20
3-rhamnosylarabinosylgalactoside†	11	62	25	13
3-rhamnosylarabinosylglucoside†	11	62	25	13
3-galactosylglucoside‡ (and/or diglucoside and digalactoside)	46	54	26	16
Quercetin				
3-glucoside†	50	23	06	37
3-α-L-arabinopyranoside‡	73	18	10	47
3-rutinoside	42	49	22	38
3-rhamnosylglucoside acylated?§	61	78	42	51
3-galactosylglucoside acylated? (1)‖	68	59	29	63
3-galactosylglucoside acylated? (2)‖	87	61	35	87
3-rhamnosylarabinosylgalactoside†	38	75	36	28
3-rhamnosylarabinosylglucoside¶	51	34	38	56
3-rhamnosylgalactosylglucoside (1)¶	21	88	70	42
3-rhamnosylgalactosylglucoside (2)¶	35	64	44	47
Isorhamnetin				
3-glucoside†	50	23	06	73
3-rhamnosylglucoside**	51	55	29	71
3-rhamnosylglucoside acylated? (1)§	65	53	78	71
3-rhamnosylglucoside acylated (2)§	89	54	83	87
Kaempferol				
3-glucoside‖	66	15	03	43
3-rhamnosylglucoside‡ + 3-rhamnosylarabinoside‡?	64	59	22	63
3-galactosylglucoside acylated? (1)‖	68	59	29	63
3-galactosylglucoside acylated? (2)‖	87	61	35	87
3-rhamnosylarabinosylgalactoside†	45	79	45	46
3-rhamnosylgalactosylglucoside†	54	77	38	56
Iso-orientin				
7-rhamnosylglucoside††	55	71	49	51
7-rhamnosylarabinosylglucoside††	46	68	44	28

*Rutin included for comparison of R_f.
†Isolated from *Klattia partita*.
‡Isolated from *Klattia stokoei*.
§Isolated from *Patersonia fragilis*.
‖Isolated from *Nivenia fruticosa*.
¶Isolated from *Nivenia stokoei*.
**Isolated from *Witsenia maura*.
††Isolated from *Gladiolus tristis*.

EXPERIMENTAL

Plant material. Verified plant material was received from various sources; see Table 1 for details.

Identification of phenolic constituents. Leaf flavonoids. Flavonoid aglycones were characterized from acid hydrolysed leaf extracts using standard procedures and in comparison with authentic markers. Direct 80% methanolic leaf extracts were run on 2D-PCs in BAW and 15% HOAc. Known glycosides isolated and purified by standard procedures were characterized on the basis of UV spectral analysis, R_f, acid hydrolysis to aglycone and sugar and where possible by direct comparison with authentic markers. Flavone *C*-glycosides were confirmed by 4 hr acid hydrolysis with 2 N HCl, extraction into *iso*-amyl alcohol and PC against vitexin in BAW and H_2O. Flavonoid sulphates were detected by paper electrophoresis of direct MeOH leaf extracts at pH 2.2 (HOAc–HCOOH buffer) for 2 hr at 400 V.

Flavonoid glycosides. The characterization of five 6-hydroxylated flavone glycosides from *Crocus* species (see Table 2) has been previously described [14]. The R_f data for some unusual flavonol di- and triglycosides listed in Table 2 are given in Table 6. In these constituents the aglycone and sugars were identified after acid hydrolysis by standard procedures. UV spectral analysis suggested that the sugars were all attached at the 3-position; however, the order of the sugars was not determined. Alkaline hydrolysis of a possible acylated isorhamnetin 3-rhamnosylglucoside (2) from *Patersonia fragilis* altered the R_f in BAW from 87 to 60 but the R_fs in 50% HOAc, Forestal and CAW (1:1) remained unchanged. R_f data of another isorhamnetin 3-rhamnosylglucoside (1) and two quercetin and kaempferol rhamnosylglucosides from *Nivenia fruticosa* suggested these compounds were also acylated but there was not sufficient material for alkaline hydrolysis.

Mangiferin and plumbagin. The identification of mangiferin, isomangiferin and plumbagin has already been described [15] in a number of Iridaceae. However, the presence of mangiferin and a mangiferin *O*-glucoside in *Lapeirousia fabricii* and plumbagin in *Phaiopleps acaule* was confirmed in the present study using the same procedures.

Biflavonoids. Biflavonoids were isolated from 80% MeOH leaf extracts by PC on 3 MM paper in BAW, where they ran near the solvent front. They were purified on TLC silica gel in toluene–HCOOEt–HCOOH (5:4:1) followed by PC on 3 MM paper in *n*-BuOH–1 M NH_4OH (1:1) or TLC on silica gel in toluene–pyridine–HCOOH (100:20:7). Details of other solvents and supports used in the separation of biflavonoids are given in Table 7.

The characterization of amentoflavone in leaves of *Patersonia glabrata* has been previously reported [15]. However, the R_f data for two constituents of the Iridaceae, 2,3-dihydroamentoflavone and an amentoflavone monomethyl ether (possibly sotetsuflavone) are given compared with some authentic markers in Table 7. 2,3-Dihydroamentoflavone was identical in R_f and UV spectral data with an authentic marker. UV λ_{max}^{MeOH} nm: 285, 325; + NaOAc 293, 315, 380; + H_3BO_3 286, 325; + NaOH 400; + $AlCl_3$ 285, 309, 350, 390; + $AlCl_3$–HCl 285, 309, 350, 390. The unknown amentoflavone monomethyl ether gave hexamethylamentoflavone on permethylation and had UV λ_{max}^{MeOH} 270, 335; + NaOAc 270, 360; + H_3BO_3 270, 335; + NaOH 400. It did not co-chromatograph with bilobetin, podocarpus A or sequoiaflavone, which suggests by elimination that it might be sotetsuflavone (the 7′-methyl ether). However, the absence of any NaOAc shift would suggest that both the 7 and 7′-positions are occupied, although the R_f data rule out a dimethyl ether. Unfortunately an authentic marker of sotetsuflavone was not available and we are awaiting more material of *Isophysis* in order to isolate sufficient of the unknown for FAB MS.

Floral flavonoids. Known anthocyanins were isolated and identified from fresh flowers by standard procedures [11]. Pigments were checked for the presence of malonyl acylation by extracting fresh tissues with MeOH–HOAc–H_2O (19:2:19) and electrophoresing the concd extracts in acetate buffer at pH 4.4 at 10 V/cm for 2 hr [41]. The only species which proved positive was *Lapeirousia corymbosa*, the flowers of which were taken from a recent herbarium specimen of one of us (PG). The purified pigment was zwitterionic and gave delphinidin and glucose on hydrolysis. The deacylated pigment was formulated as delphinidin 3-diglucoside on the basis of spectral and R_f properties. R_f values (× 100) for the acylated pigment, the deacylated pigment and delphinidin 3-glucoside were: in BAW, 40, 25 and 26; in 1% HCl, 06, 08 and 03; and in 15% HOAc–HCl, 30, 34 and 16. Fresh petals of a *Sisyrinchium* species yielded two rare petunidin glycosides, the 3-diglucosylrhamnoside and the 3-rutinoside. These were so formulated on the basis of spectral measurements, partial hydrolysis and R_f data. R_f values (× 100)

Table 7. R_f (× 100) data for some biflavonoids found in the Iridaceae*

Biflavonoid	Silica gel TEF (5:4:1)	Silica gel TPF (100:20:7)	Cellulose BN (1:1)	Solvents Polyamide 11 T–MEK–MeOH (4:3:3)	Microcrystalline polyamide Nitromethane–MeOH (4:3)
Amentoflavone†‡	40	04	33	06	05
7-Methyl ether (sequoiaflavone)	40	04	28	09	05
4′-Methyl ether (Podocarpus A)	47	09	64	15	21
4″-Methyl ether (bilobetin)	47	10	27	36	44
Unknown methyl ether from *Isophysis tasmanica*	47	09	64	16	46
2,3-Dihydroamentoflavone from *Isophysis tasmanica*	45	04	31	18	14
2,3-Dihydroamentoflavone	45	04	31	18	14
Hinokiflavone	47	07	16	12	08
Ginkgetin	50	21	74	—	—

*Other biflavonoids are included for comparison.

†Identified in *Isophysis tasmanica.*

‡Identified in *Patersonia glabrata.*

Key: T = toluene, E = ethyl formate, F = formic acid, B = *n*-butanol, N = 1 M ammonia, MEK = methyl ethyl ketone.

for the 3-triglycoside, the 3-rutinoside and petunidin 3-glucoside were: in BAW, 56, 36 and 39; in 1% HCl, 30, 15 and 08; and in 15% HOAc–HCl, 56, 42 and 30.

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