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ANTHOCYANIN PIGMENTS AND LEAF FLAVONOIDS IN THE FAMILY ARACEAE

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Abstract—Anthocyanins, variously identified in inflorescence, fruit, leaf or petiole of 59 representative species of the Araceae, are of a simple type. The most common pigment is cyanidin 3-rutinoside, while pelargonidin 3-rutinoside and cyanidin 3-glucoside are regularly present. Two rare pigments are: cyanidin 3-gentiobioside in *Anchomanes* and *Rhektophyllum*, both in the subfamily Lasioideae; and delphinidin 3-rutinoside in *Schismatoglottis concinna*. In a leaf survey of 144 species from 58 genera, flavone *C*-glycosides (in 82 %) and proanthocyanidins (in 35–45 %) were found as the major flavonoids. In the subfamily Calloideae, subtribe Symplocarpeae, flavonols replace glycoflavones as the major leaf components but otherwise flavonols are uncommon in the family (in 27 % of the sample) and more usually co-occur with flavone *C*-glycosides. Two new flavonol glycosides were characterized from *Lysichiton camtschatcense*: kaempferol 3-(6-arabinosylgalactoside) and kaempferol 3-xylosylgalactoside. Simple flavones, luteolin and chrysoeriol (in 6 %) were found only in the subtribes Arinae and Cryptocoryninae, subfamily Aroideae. Flavonoid sulphates were identified in only four taxa: glycoflavone sulphates in two *Culcasia* species and *Philodendron ornatum* and a mixture of flavone and flavonol sulphates in *Scindapsus pictus*. Caffeic ester sulphates were more common and their presence in *Anthurium hookeri* was confirmed. These results show that the Araceae are unusual amongst the monocots in their simple and relatively uniform flavonoid profile; no one subfamily is clearly distinguished, although at tribal level some significant taxonomic patterns are observed. The best defined groups are the subfamilies Lasioideae and Monsteroideae, and the tribes Symplocarpeae and Arophyteae, and the subtribe Arinae. The greatest chemical diversity occurs in *Anthurium* and *Philodendron*, but this may only reflect the fact that these are the two largest genera in the family. The origin and relationship of the Araceae to other monocot groups are discussed in the light of the flavonoid evidence.

INTRODUCTION

The Araceae, a family of some 110 genera and over 2000 species are distributed largely in the tropics and subtropics, but a few taxa (e.g. *Arum*) are found in temperate zones. Members of the Araceae exhibit a wide variety of vegetative habit; many species, particularly those of higher latitudes, are acaulescent herbs with underground tubers or rhizomes, but in the tropics the family is often represented predominantly by climbers and epiphytes, while woody and aquatic species also occur. Such diversity of habit makes the family difficult to classify and most systems employ both anatomical and morphological characteristics. Genera have been variously grouped into a number of subfamilies or tribes; in the present study the results are arranged according to Bogner's [1] recent modification of Engler's classic system [2], in which eight subfamilies and 31 tribes are recognized.

Despite the economic importance of those aroids with edible rhizomes (e.g. *Colocasia*) and a diversity of uses by indigenous cultures in the tropics, the family has not been studied extensively for its chemical constituents. Thus, Hegnauer [3] records saponins, cyanogenic compounds and polyphenols from only a small number of species. Bate-Smith [4] in his leaf flavonoid survey of the monocotyledons, examined 24 members of the Araceae. He identified quercetin in eight, kaempferol in six and procyanidin in eleven species, respectively, but he regarded the family as being very diverse in phenolic pattern, because of the presence of many further uncharacterized constituents. We have reported previously [5] the presence of kaempferol 3-sophoroside-7-rhamnoside from *Gymnostachys anceps* and more recently Zennie and McClure [6] have isolated vitexin, orientin, two flavone di-*C*-glycosides, a luteolin 7-glycoside and cyanidin 3-glucoside from the free floating aquatic, *Pistia stratiotes*. In a detailed study of *Arum maculatum* Koch and Steinegger [7] have characterized apigenin, luteolin, luteolin 7-glucoside, quercitrin, rutin, orientin, isoorientin, vitexin, isovitexin, saponarin, *p*-coumaric, caffeic and chlorogenic acids from leaves and berries. Anthocyanins have only been reported from the spathe of *Anthurium scherzerianum* (pelargonidin 3-rutinoside) [8], the spathe of *A. andraeanum* (cyanidin and pelargonidin 3-rutinoside) [9] and the spathe and spadix of *Symplocarpus foetidus* (cyanidin 3-rutinoside, peonidin 3-rutinoside and cyanidin 3-glucoside) [10].

The present investigation follows recent studies of the Orchidaceae [11], Restionaceae [12] and Commelinaceae (M. A. Del Pero de Martinez, unpublished results), and forms part of a larger flavonoid survey of monocotyledonous families, which is now almost complete.

RESULTS

Anthocyanins

Anthocyanins occur in the bright scarlet to mauve fruits of members of the Araceae, and are presumably important for providing attractive coloration for purposes of seed dispersal. These pigments are also evident in the flowering parts, e.g. in the purplish red on spathe and spadix in *Arum*, although the major pollinators are beetles and flies, which are essentially attracted to the flower by the often evil-smelling odours produced in the inflorescence. Red to purple-black coloration is also present in leaf petioles in many species; occasionally, this colour occurs in the epidermis of the leaf (e.g. in *Xanthosoma violaceum*, *Alocasia cuprea*). In the present survey, it was possible to detect anthocyanin in just under half the species available for flavonoid studies. In all, 60 species representing half the tribes and five of the seven subfamilies were examined. The results are shown in Table 1.

In keeping with the observation that there is little natural selection for flower colour in this family due to the activities of pollinators with colour vision, it was found that the major anthocyanidin is cyanidin. It was present in every species, except *Schismatoglottis concinna*, where it was replaced by delphinidin. Pelargonidin was found to accompany cyanidin in eight taxa: five *Anthurium* species, in two *Dracontium* species and in *Xanthosoma helleborifolium*. In *Anthurium affine* and *A. gracile*, pelargonidin is in the fruit skin and is presumably responsible in part for the bright scarlet coloration in these two species.

The anthocyanidins of the Araceae are nearly always present as the 3-rutinoside. Thus, cyanidin 3-rutinoside is by far the most common pigment (Table 1), being accompanied in some cases by the related 3-glucoside. Exceptionally, cyanidin 3-gentiobioside was found to replace the 3-rutinoside in two taxa: in the fruit of *Anchomanes abbreviatus* and in the petiole of *Rhektophyllum mirabile*. This finding is of great interest as there are cytological and morphological grounds for placing *Anchomanes* in the tribe Nephthytideae rather than the Pythonieae, and this chemical evidence supports such a view. Since gentiobiosides are uncommon in the anthocyanin series, the pigment was fully characterized and the gentiobiose released by H_2O_2 oxidation compared directly with authentic material; this represents the first characterization of cyanidin 3-gentiobioside in the Monocotyledoneae. However, the related pelargonidin glycoside is known from *Tritonia* cv Prince of Orange (Iridaceae) [13] and the delphinidin derivative from *Eichhornia crassipes* (Pontederiaceae) [14].

Wherever different tissues (spathe and spadix or petiole and leaf) were examined in the same species, the same pigments were generally found to be present. However, there is some variation in the nature of fruit coloration in the family, since anthocyanin is very occasionally replaced by carotenoid. Indeed in the fruits of *Arum maculatum* where the spathe and spadix contain cyanidin 3-rutinoside and cyanidin 3-glucoside, anthocyanins are absent, the red coloration being due to several carotenoids [15]. The only other source of carotenoid fruit coloration observed in the present survey was *Arisaema flavum*. There may be a taxonomic element in whether red fruit coloration is due to carotenoids, since both *Arum* and *Arisaema* are in the same tribe of the Aroideae.

Flavonols

The results of the leaf flavonoid survey are shown in Table 2, both fresh and herbarium leaf tissue being used. The data in Table 2 refer to flavonoid aglycones, which were detected in leaf tissue after acid hydrolysis. The aglycones were characterized by comparison of R_f values and colour reactions in UV light with standard markers. These results were confirmed by 2D-PC of direct leaf extracts and by the identification of the flavonoid glycosides in ten species (Table 3). The presence of flavone *C*-glycosides was confirmed by their resistance to acid hydrolysis and the direct leaf extracts were screened for flavonoid sulphates by paper electrophoresis at pH 2.2.

During the course of the survey two new flavonol glycosides were characterized from leaf tissue of *Lysichiton camtschatcense* (subfamily Calloideae, tribe Symplocarpeae): kaempferol 3-(6-arabinosylgalactoside) and kaempferol 3-xylosylgalactoside. Quercetin 3-(6-arabinosylgalactoside) recently reported for the first time from *Hydrocotyle vulgaris* (Hydrocotylaceae) [16] was also identified in *L. camtschatcense* together with traces of what is probably the corresponding isorhamnetin derivative. Flavonols were also the predominant constituents in leaves of the two other members of the tribe Symplocarpeae: *Orontium aquaticum* and *Symplocarpus foetidus*. In *O. aquaticum* a complex mixture of quercetin and isorhamnetin 3-galactosides, quercetin and kaempferol 3-galactosylglucosides (or glucosylgalactosides) and isorhamnetin 3-rhamnosylgalactoside (or galactosylrhamnoside) was found. In *S. foetidus* two quercetin and two kaempferol glycosides also gave galactose and glucose on acid hydrolysis; two of these compounds have similar R_f values to the quercetin and kaempferol galactosylglucosides present in *O. aquaticum*, the other glycosides may be acylated derivatives. *Calla palustris*, the only member of the Calleae, the other tribe in the Calloideae, has a very different flavonoid pattern, in which flavone *C*-glycosides predominate and flavonols are absent. Indeed in the family as a whole flavonols were found in only 27% of the species surveyed, were frequent constituents in only two other subfamilies: the Colocasioideae (in 55% of the sample) and the Philodendroideae (in 40% of the sample), and were not detected in any members of the Lasioideae or in *Pistia stratiotes*.

Flavone C-glycosides

The most characteristic flavonoid constituents of the Araceae are flavone *C*-glycosides (found in 82% of the species surveyed), which were the major leaf components in six of the eight subfamilies: in the Pothoideae (in 76%), Lasioideae (in 100%), Philodendroideae (in 87%), Colocasioideae (in 100%), Aroideae (in 86%) and in the Pistioideae (1 out of 1 species). Flavone mono-*C*- and di-*C*-glycosides and *O*-glycosyl derivatives were all represented. A number of flavone *C*-glycosides were characterized during the survey (see Table 3). Orientin, isoorientin and isovitexin were identified in leaves of *Arum*

Table 1. Anthocyanins identified in the Araceae

Subfamily, tribe*, genus, species	Plant source†	Accession no. or collector's name and no.	Organ‡	Anthocyanins§ Pg 3RG	Cy 3RG	Cy 3Glc	Other
Pothoideae							
Anthurieae							
Anthurium affine Schott	K	166-77.06061	F	+	+	−	−
A. bakeri Hook. f.	K	000-73.13098	F, Sx	−	+	−	−
A. bellum Schott	K	131-74.01527	Sx	+	+	−	−
A. erskinei Mayo	K	106-77.00900	Sx, Sp	−	+	−	−
A. galeottii C. Koch	K	171-77.01429	Sp	+	+	+	−
A. gladiifolium Schott	K	078-77.06055	Sx	−	+	−	−
A. gracile (Rudge) Lindl.	K	230-73.02176	F	+	+	−	−
Anthurium sp. nov ('harleyi')	K	166-77.01345	Sx	−	+	−	−
A. inconspicuum N. E. Brown	K	171-77.01436	Sx, Sp	+	+	−	−
A. jilekii Schott	K	078-77.00734	Sx	−	+	−	−
A. longifolium (Hoffmannsegg) Kunth	K	078-77.00700	Sx, Sp	−	+	−	−
A. miquelianum C. Koch & Augustin	K	171-77.01428	P, Sx	−	+	−	−
Anthurium sp. nov. ('talmonii')	K	106-77.00976	Sx	−	+	−	−
A. radicans C. Koch & Haage	K	513-77.05366	P	−	+	−	−
A. regale Linden	K	000-73.13127	Sx	−	+	−	−
A. salvimae Hemsley	K	664-61.66404	F	−	+	−	−
A. schlechtendalii Kunth	K	000-69.19884	F	−	+	−	−
Lasioideae							
Lasieae							
Dracontium asperum C. Koch	K	513-77.05372	P	+	+	−	−
D. foecundum Hook. f.	K	568-63.56802	Sx, Sp	+	+	−	−
Pythonieae							
Amorphophallus abyssinicus (A. Rich.) N. E. Brown	K	741-64.74101	Sp	−	+	−	−
A. stuhlmannii (Engl.) Engl. & Gehrm.	K	006-75.0045	Sp	−	+	−	−
Anchomanes abbreviatus Engl.	K	518-52.51801	F	−	−	−	Cy and Pg gentiobioside & Pg-3Glc
Nephthytideae							
Rhektophyllum mirabile N. E. Brown	K	000-73.13156	P	−	−	+	Cy 3-gentiobioside
Philodendroideae							
Philodendreae							
Homalomeninae							
Homalomena rubescens (Roxb.) Kunth	K	382-68.38220	L, P	−	−	+	−
Schismatoglottidinae							
Schismatoglottis concinna Schott var. *immaculata* N. E. Brown	K	000-73.13208	L, P	−	−	−	Dp 3-rutinoside
Philodendrinae							
Philodendron near *burle-marxii* G. M. Barroso	K	019-75.00098	L	−	+	−	−
P. erubescens C. Koch & Augustin	K	000-73.13163	Sx, Sp, P	−	+	+	−
P. insigne Schott	K	174-78.01616	L	−	+	−	−
P. linnaei Kunth	K	078-77.00667	L	−	+	−	−
P. melinonii Brongn.	K	174-78.01530	L	−	−	+	−
P. ornatum Schott	K	078-77.00722	L	−	−	+	−
P. squamiferum Poepp.	K	000-73.13198	P	−	+	−	−

Table 1. *(Continued)*

Subfamily, tribe*, genus, species	Plant source†	Accession no. or collector's name and no.	Organ‡	Anthocyanins§			
				Pg 3RG	Cy 3RG	Cy 3Glc	Other
P. verrucosum Mathieu ex Schott	K	000-73.13200	L, P	−	+	+	−
Philodendron sp.	K	062-73.00381	St	−	+	+	−
Philodendron sp.	K	393-74.03059	Sx, Sp	−	−	+	−
Typhonodoreae							
Typhonodorum lindleyanum Schott	K	000-73.19138	L	−	+	+	−
Colocasioideae							
Colocasieae							
Caladiinae							
Caladium bicolor (Ait.) Vent.	K	No number	L	−	+	−	−
Xanthosoma helleborifolium (Jacq.) Schott	K	513-77.05353	St	+	+	−	−
X. violaceum Schott	K	322-70.03043	P	−	+	−	−
	K	455-63.45516	L	−	+	−	−
	K	576-65.57607	L	−	+	−	−
Xanthosoma sp. nov.	K	513-77.05380	St	−	+	−	−
Alocasiinae							
Alocasia cuprea (C. Koch & Bouché) C. Koch	K	514-58.51404	L	−	+	−	−
	K	457-63.45701	L	−	+	−	−
A. macrorrhiza (L.) G. Don var. *rubra* (Hassk.) Furtado	K	209-55.20907	P	−	+	−	−
A. macrorrhiza (L.) G. Don var. *variegata* (Schott) Furtado	K	382-68.38217	P	−	+	−	−
A. portei Schott	K	367-79.03381	P	−	+	−	−
A. thibautiana Mast. cv Silver King	K	484-52.48403	L	−	+	−	−
Alocasia sp.	K	000-73.13094	L	−	+	−	−
Xenophya lauterbachiana (Engl.) Nicolson	K	253-57.25302	L, St	−	+	−	−
Aroideae							
Stylochitoneae							
Stylochiton sp. aff. *maximus* Engl.	K	301-68.30106	St	−	+	−	−
S. lancifolius Kotschy & Peyr.	K	869-59.86901	St	−	+	−	−
Asterostigmateae							
Asterostigma riedelianum (Schott) O. Kuntze	K	106-77.00963	St	−	+	+	−
Areae							
Arinae							
Arum maculatum L.	RNG‖		Sx, Sp	−	+	+	−
Dracunculus canariensis Kunth	RNG	Jarvis Murphy 229 Hierro Valverde Guarazoco Rd 3 km from Valverde	Sp	−	+	+	−
Helicodiceros muscivorus (L. f.) Engl.	RNG‖		Sp	−	+	−	−
Typhonium giraldii (Baroni) Engl.	K	Cult. S. Mayo	St	−	+	−	−
Arisaematinae							
Arisaema flavum (Forssk.) Schott	K	409-77.03159	F	−	−	−	−
Arisaema sp.	K	047-79.00345	P	−	+	+	−
Pinelliinae							
Pinellia tripartita (Blume) Schott	K	Cult. S. Mayo	St	−	+	−	−

* Classification according to Engler [2] with modifications by Bogner [1].

† Plant sources: K = plants growing at the Royal Botanic Gardens, Kew, for which voucher specimens have been deposited in the herbarium (K); RNG = Reading University Herbarium; and RNG‖ = plants growing at the Botany Department, University of Reading (voucher specimens are deposited in RNG).

‡ Key to organs: F = fruit, Sx = spadix, Sp = spathe, St = stem, L = leaf and P = petiole.

§ Key to anthocyanins: P = pelargonidin, C = cyanidin, Dp = delphinidin, RG = rutinoside and Glc = glucoside.

Table 2. The distribution of flavonoids in leaves of the Araceae

Subfamily, tribe*, subtribe, genus, species	Flavone *C*-glycosides	Flavonols	Flavones	Proantho-cyanidins	Plant source†	Accession no. or collector's name and no.
Pothoideae						
Pothoeae						
Pothos scandens L.‖	–	–	–	–	K	000-69.51673
Heteropsideae						
Heteropsis salicifolia Kunth	–	–	–	–	K‡	R. S. Pinheiro & T. S. Santos 2266 8 km on road BR101 from Linhares to Vitoria, Espirito Santo, Brazil
Anthurieae						
Anthurium bakeri Hook. f.‖	(+)	–	–	–	K	000-73.13098
A. bellum Schott§	+	–	–	Cy	K	131-74.01527
A. clavigerum Poepp.	+	–	–	–	K	703-60.70303
A. cordatum (L.) G. Don	+	–	–	–	K	029-78.00156
A. erskinei Mayo	+	–	–	–	K	106-77.00900
A. galeottii C. Koch‖	+	–	–	–	K	171-77.01429
A. gladiifolium Schott	+	(Qu) (Km)	–	Cy	K	078-77.06055
A. gracile (Rudge) Lindl.§	–	–	MF	Cy	K	230-73.02176
A. sp. nov. ('harleyi')	+	–	–	–	K	166-77.01345
A. hookeri Kunth§‖	–	–	–	Cy	K	422-74.03515
A. inconspicuum N. E. Brown	+	–	–	–	K	171-77.01436
A. lindmanianum Engl.	+	–	–	Cy	K	500-65.50022
A. longifolium (Hoffmannsegg) Kunth	+	–	–	–	K	078-77.00700
A. miquelianum C. Koch & Augustin‖	+	–	–	–	K	171-77.01428
A. pedatoradiatum Schott¶	+	–	–	–	K	504-69.04135
A. pentaphyllum (Aubl.) G. Don‖¶	+	(Qu) (Km)	–	Cy	K	106-77.00949
	+	(Km)	–	–	K	277-66.27701
	+	Qu, Km	–	Cy	K	078-77.00757
A. polyschistum R. E. Schult. & Idrobo	–	–	MF	–	K	206-76.01533
	–	–	MF	–	K	062-73.00368
A. radicans C. Koch & Haage	–	Qu, Km	–	Cy	K	513-77.05366
A. regale Linden¶	+	–	–	(Cy)	K	000-73.13121
	+	(Qu)	–	Cy	K	000-73.13127
A. scandens (Aubl.) Engl.	+	–	–	–	K	106-77.00995
A. wendlingeri G. M. Barroso	–	–	–	–	K	196-76.01509
Culcasieae						
Culcasia saxatilis A. Chev.¶,‖	+	–	–	–	K	050-65.05001
Culcasia sp.¶	+	–	–	–	K	052-69.00476

Table 2. (*Continued*)

Subfamily, tribe*, subtribe, genus, species	Flavone *C*-glycosides	Flavonols	Flavones	Proantho-cyanidins	Plant source†	Accession no. or collector's name and no.
Zamioculcaseae						
Gonatopus boivinii (Decne.) Hook. f.¶,§	+	–	–	–	K	301-68.30105
	+	–	–	–	K	735-33.73501
G. rhizomatosus Bogner & Oberm.	+	–	–	–	K	272-71.02486
Zamioculcas lanceolata A. Peter	+	–	–	–	K	494-67.49404
Z. zamiifolia (Lodd.) Engl.	(+)	–	–	–	K	349-63.34902
Acoreae						
Acorus calamus L.	+	–	–	–	RNG	J. E. Lousley V.C. 17. 14 July 1956, St. Georges Way, Wolworth, Surrey
Monsteroideae						
Monstereae						
Amydrium sp.‖	+	–	–	–	K	455-63.45517
Epipremnum, pinnatum (L.) Engl.¶,‖	–	–	–	–	K	685-69.06334
E. pinnatum (L.) Engl. cv Aureum‖	–	–	–	–	K	029-78.00158
Monstera lechleriana Schott forma‖	–	–	–	–	K	671-62.67115
Rhaphidophora africana N. E. Brown	–	–	–	–	K	104-76.00787
Scindapsus pictus Hassk.‖,§	–	Qu	Chrys	–	K	145-76.01047
	–	Qu	Chrys	–	K	145-76.01046
Scindapsus sp.§	+	–	–	–	K	431-63.43108
Scindapsus sp.§	+	–	–	–	K	455-63.45521
Scindapsus sp.	(+)	–	–	–	K	477-75.05026
Stenospermation marantifolium Hemsl.‖	–	–	–	–	K	567-62.56708
Spathiphylleae						
Holochlamys beccarii Engl.‖	–	–	–	–	K	160-70.01474
Spathiphyllum cannifolium (Dryand.)‖ Schott	+	–	–	–	K	423-74.03588
Calloideae						
Symplocarpeae						
Lysichiton camtschatcense (L.) Schott	–	Qu, Km, Isorh	–	–	K	364-36.36401
Orontium aquaticum L.	–	Qu, Km, Isorh	–	–	K	000-69.19635
Symplocarpus foetidus (L.) Salisb.	–	Qu, Km	–	–	K	000-69.18003
Calleae						
Calla palustris L.	+	–	–	Cy	K	307-76.03028
Lasioideae						
Lasieae						
Lasiinae						
Cyrtosperma johnstonii (Bull) N. E. Brown	+	–	–	Cy?	K	000-73.13139

Dracontium asperum C. Koch¶	+	–	–	–	K	513-77.05372
D. foecundum Hook. f.	+	–	–	–	K	568-63.56802
Pycnospathinae						
Pythonieae						
Amorphophallus stuhlmannii (Engl.) Engl. & Gehrm.	+	–	–	–	K	006-75.00045
Anchomanes difformis (Blume)¶,§ Engl. Nephthytideae	+	–	–	Cy	K	386-61.38601
Cercestis afzelii Schott¶	+	–	–	Cy	K	699-58.69903
C. congensis Engl.	+	–	–	Cy	K	040-70.00388
Rhektophyllum mirabile N. E. Brown	+	–	–	Pel	K	000-73.13156
Montrichardieae						
Philodendriodeae						
Philodendreae						
Homalomeninae						
Homalomena coerulescens Jungh.‖ ex Miq.	+	–	–	Cy	K	000-73.13144
H. rubescens (Roxb.) Kunth	+	(Qu)	–	Cy?	K	382-68.38220
H. rubra Hassk.	–	–	–	–	RNG	Chin 6 July 1967, Taiping, Malay Peninsula map ref, 2M/4
Schismatoglottidinae						
Schismatoglottis concinna Schott var. *immaculata* N. E. Brown‖	+	Qu, Isorh	–	Cy	K	000-73.13208
Philodendrinae						
Philodendron auriculatum Standl. & L. O. Williams	+	–	–	Cy	K	434-59.43410
P. near *burle-marxii* G. M. Barroso	–	Qu	–	Cy?	K	019-75.00098
P. crassinervium Lindl.‖	+	Qu (Km) (Isorh)	–	Cy	K	513-77.05363
P. eichleri Engl.	+	–	–	Cy	K	000-73.13165
P. erubescens C. Koch & Augustin‖	+	(Qu)	–	Cy?	K	000-73.13163
P. goeldii G. M. Barroso	+	–	–	Cy	K	300-79.02602
P. imbe Schott	+	–	–	Cy	K	106-77.00895
P. inaequilaterum Liebm.	–	–	–	–	K	365-64.36504
P. insigne Schott‖	+	Qu, Km	–	Cy	K	174-78.01616
P. leal-costae Mayo & G. M. Barroso	+	Qu, Km	–	Cy	K	106-77.01004
P. linnaei Kunth	+	(Qu) (Km)	–	Cy	K	078-77.00667
P. longilaminatum Schott	+	(Qu) (Km)	–	Cy	K	078-77.00767
P. melanochrysum Linden & André	+	–	–	Cy	K	318-60.31804
P. melinonii Brongn.	+	Qu, (Isorh)	–	Cy?	K	174-78.01530
P. ornatum Schott.§	+	–	–	Cy?	K	078-77.00722
P. pachyphyllum K. Krause	+	(Qu)	–	–	K	106-77.00936
P. pedatum (Hook.) Kunth	+	–	–	Cy	K	001-70.00019
	+	(Qu)	–	Cy	K	125-74.01418
	(+)	Qu	–	Cy?	K	386-71.03631
P. radiatum Schott‖	+	–	–	Cy	K	000-73.13204
P. saxicolum K. Krause	+	Qu Isorh?	–	Cy	K	059-74.00782

Table 2. (*Continued*)

Subfamily, tribe*, subtribe, genus, species	Flavone C-glycosides	Flavonols	Flavones	Proantho-cyanidins	Plant source†	Accession no. or collector's name and no.
P. scandens C. Koch & H. Sello‖	+	–	–	Cy	K	000-73.13193
P. scandens C. Koch & H. Sello subsp. *prieurianum* (Schott) Bunting	+	–	–	Cy	K	187-75.01916
P. simsii (Hook.) G. Don	–	–	–	Cy	K	000-73.13195
P. smithii Engl.	+	–	–	Cy	K	473-69.03905
P. speciosum Schott‖	+	–	–	–	K	171-77.01448
P. squamiferum Poepp.	+	–	–	Cy?	K	000-73.13198
Philodendron sp.§	+	–	–	Cy?	K	062-73.00381
Philodendron sp.	+	Qu Isorh	–	Cy	K	393-74.03059
Philodendron sp.§	+	Qu	–	Cy	K	651-60.65102
Anubiadeae						
Anubias lanceolata N. E. Brown	+	–	–	Cy	K	022-63.02202
Aglaonemateae						
Aglaonema modestum Schott ex Engl.	(+)	–	–	Cy	RNG‡	
Aglaonema sp.	+	–	–	Cy	K	200-68.20002
Dieffenbachieae						
Dieffenbachia oerstedii Schott¶	–	–	–	–	K	000-69.11744
Zantedeschieae						
Zantedeschia aethiopica (L.) Spreng.	+	–	–	–	K	533-51.53301
Typhonodoreae						
Typhonodorum lindleyanum Schott	+	–	–	Cy	K	438-79.04434
Peltandreae						
Peltandra virginica (L.) Kunth	+	(Qu)	–	Cy	K	000-69.19636
Colocasioideae						
Colocasieae						
Remusatia vivipara (Lodd.) Schott¶	+	–	–	–	K	577-69.05188
Steudnerinae						
Hapalininae						
Caladiinae						
Caladium bicolor (Ait.) Vent.¶	+	–	–	–	K	681-69.06199
	+	(Qu)	–	–	K	No number
Xanthosoma brasiliense (Desf.) Engl.	+	(Qu)	–		K	797-58.79707
X. helleborifolium (Jacq.) Schott	+	–	–	–	K	513-77.05354
X. aff. *robustum* Schott¶	+	–	–	Cy	K	175-78.01749
X. sagittifolium (L.) Schott¶	+	–	–	Cy	RNG‡	
X. violaceum Schott¶	+	–	–	Cy?	K	455-63.45516
	+	–	–	Cy?	K	576-65.57607
	+	Qu	–	Cy?	K	322-70.03043

Xanthosoma sp. *nov.*	+	Qu	–	Cy?	K	513-77.05380
Colocasiinae						
Colocasia esculenta (L.) Schott[‖,¶]	+	Qu	–	Cy?	K	035-79.00180
	+	–	–	Cy	RNG[‡]	
C. indica (Lour.) Hassk.	+	–	–	Cy	K	412-77.03382
Alocasiinae						
Alocasia cf. *alba* Schott	+	(Km)	–	–	K	514-58.51406
A. cuprea (C. Koch & Bouché)[¶] C. Koch	–	Qu, Km	–	Cy?	K	514-58.51404
	(+)	Qu, (Km)	–	Cy?	K	457-63.45701
A. cucullata (Lour.) G. Don[¶]	+	–	–	–	K	434-63.43404
A. macrorrhiza (L.) G. Don var. *rubra* (Hassk.) Furtado[¶]	+	Qu	–	Cy	K	209-55.20907
A. macrorrhiza (L.) G. Don var. *variegata* (Schott) Furtado[¶]	+	(Km)	–	–	K	687-61.68703
	+	(Qu)	–	Cy	K	382-68.38217
A. odora (Roxb.) C. Koch[¶]	+	–	–	Cy	K	263-58.26301
A. portei Schott[¶]	+	–	–	–	K	367-79.03381
A. thibautiana Mast. cv Silver King[¶]	+	Qu (Km)	–	Cy?	K	484-52.48403
Xenophya lauterbachiana (Engl.)[¶] Nicolson	+	Qu	–	Cy?	K	253-57.25302
Syngonieae						
Syngonium auritum (L.) Schott[¶]	+	–	–	Cy	K	000-73.13215
S. podophyllum Schott	+	–	–	–	K	000-73.13217
Ariopsideae						
Aroideae						
Stylochitoneae						
Stylochiton borumensis N. E. Brown[‖]	–	Qu	–	–	K	100-67.10001
S. lancifolius Kotschy & Peyr.[‖]	–	Qu, Km	–	Cy	K	869-59.86901
Stylochiton sp. aff. *maximus* Engl.[¶]	–	Qu, My	–	–	K	301-68.30106
S. puberulus N. E. Brown[‖]	–	–	–	–	K	231-56.23101
Arophyteae						
Arophyton buchetii Bogner	+	–	–	–	B	207
A. crassifolium (S. Buchet) Bogner	+	–	–	Cy	B	278
A. humbertii Bogner	+	–	–	–	B	160
Carlephyton diegoense Bogner	+	–	–	–	B	234
C. glaucophyllum Bogner	+	–	–	Cy	B	167
C. madagascariense Jumelle emend. S. Buchet	+	–	–	Cy	B	279
Colletogyne perrieri S. Buchet	+	–	–	–	B	165
Asterostigmateae						
Asterostigma riedelianum (Schott) O. Kuntze	+	–	–	–	K	106-77.00963
Spathiacarpa sagittifolia Schott[¶]	+	–	–	–	K	513-77.05357
Protareae						
Protarum sechellarum Engl.	+	–	–	–	K	301-73.04136

Table 2. (*Continued*)

Subfamily, tribe*, subtribe, genus, species	Flavone *C*-glycosides	Flavonols	Flavones	Proantho-cyanidins	Plant source†	Accession no. or collector's name and no.
Callopsideae						
Callopsis volkensii Engl.	+	–	–	–	K	301-68.30104
Zomicarpeae						
Areae						
Arinae						
Arum italicum Mill.	+	–	Lu, Chrys	–	RNG	J. E. Lousley V.C. 13, 20 May 1933, Swanborne Lake, Arundel, W. Sussex
A. italicum Mill. subsp. *neglectum* (Townsend) Prime	+	–	Chrys	–	RNG	E. Guinea 453, Villaviciosa, Asturias, Spain
A. maculatum L.	+	–	Lu, Chrys	–	RNG	H. Dunton 81, Nr. Westerham, Kent, map ref. ord. survey TQ 4061
Biarum tenuifolium (L.) Schott	+	–	Lu, Chrys	Cy?	RNG	E. A. Leadlay & B. Petty 208, Huelva, 3 miles S. of Aracena on N433 road
Dracunculus canariensis Kunth	+	–	Lu, Chrys	–	RNG	Jarvis & Murphy 229, Hierro Valverde, Guarazoco Rd., 3 km from Valverde
Helicodiceros muscivorus (L. f.) Engl.	+	–	–	–	RNG‡	
Sauromatum venosum (Ait.) Kunth	+	–	–	–	K	339-62.33902
Typhonium giraldii (Baroni) Engl.	+	–	Lu, Chrys	–	K	Cult. S. Mayo

Arisarinae						
Arisarum vulgare Targ. Tozz.	+	–	–	–	RNG	E. Guinea, 23 April 1941, Arrejo del Abel far Budújat Faber
Arisaematinae						
Arisaema leschenaultii Blume	+	–	–	–	K	698-69.06516
Arisaema sp.¶	+	–	–	–	K	047-79.00345
Pinelliinae						
Pinellia tripartita (Blume) Schott	+	–	–	–	K	Cult. S. Mayo
Ambrosininae						
Cryptocoryninae						
Cryptocoryne wendtii de Wit	+	–	Chrys	–	K	334-70.03260
Pistioideae						
Pistia stratiotes L.	+	–	–	?	RNG	N. Ajam, 18 August 1975, WRO, Oxford

Key: Qu = quercetin; Km = kaempferol; My = myricetin; Isorh = isorhamnetin; Lu = luteolin; Chrys = chrysoeriol; Cy = cyanidin; Pel = pelargonidin; + = present; – = absent; (+) = trace constituent; MF = probably 4′-methylated flavone(s): acacetin has been identified as such in *A. polyschistum* (K. R. Markhams, pers. comm.).

* Classification according to Engler [2] with modifications by Bogner [1].

† Plant sources: K = plants growing at the Royal Botanic Gardens, Kew, for which voucher specimens have been deposited in K‡; K‡ = the Herbarium, the Royal Botanic Gardens, Kew; RNG = Reading University Herbarium; RNG‡ = plants growing at the Botany Department, University of Reading (voucher specimens deposited in RNG); B = plant material supplied by J. Bogner, München, W. Germany.

§ Dark to dark or dark to yellow (in UV + NH_3) negatively charged compound present.

‖ Blue to blue green (in UV + NH_3) negatively charged compound present.

¶ Pale blue to intense blue (in UV and with NH_3) negatively charged compound present.

Table 3. Flavonoid glycosides identified in the leaves of some Araceae species

Species	Flavonoid glycosides identified
Anthurium bellum	Apigenin 6-*C*-arabinoside-8-*C*-glucoside (isoschaftoside) and apigenin 6-*C*-glucoside-8-*C*-arabinoside (schaftoside)
Arum maculatum	Luteolin and chrysoeriol 7-glucosides, orientin, isoorientin, isovitexin, an apigenin and a luteolin di-*C*-glycoside
*Asterostigma riedelianum**	6,8-Di-*C*-arabinosylapigenin 7,4′-dimethyl ether, 2″-*O*-glucosyl-6-*C*-arabinosylapigenin 7,4′-dimethyl ether, 2″-*O*-(caffeoyl) glucosyl-6-*C*-arabinosylapigenin 7,4′-dimethyl ether and the 7-monomethyl ethers of the mono-*C*-arabinosides
Dracontium asperum	Vitexin *O*-glucoside, isovitexin *O*-xyloside
Lysichiton camtschatcense	Quercetin, kaempferol and isorhamnetin 3-(6-arabinosylgalactoside), kaempferol 3-xylosylgalactoside
Orontium aquaticum	Quercetin and isorhamnetin 3-galactosides, quercetin and kaempferol 3-galactosylglucosides (or -glucosylgalactosides), isorhamnetin 3-rhamnosylgalactoside (or galactosylrhamnoside)
Philodendron eichleri†	Schaftoside, isoschaftoside, orientin and isoorientin
P. saxicolum	Quercetin and isorhamnetin 3-glucosides and 3-rutinosides, luteolin mono-*C*-glycoside, luteolin and apigenin di-*C*-glycosides
P. smithii	Schaftoside and isoschaftoside
Symplocarpus foetidus	Quercetin and kaempferol galactosylglucosides (or glycosylgalactosides), possible acylated derivatives of these glycosides and a kaempferol 3-diglucoside

* Results previously reported in ref. [17].
† Markham, K. R., unpublished results.

maculatum, vitexin x″-*O*-glucoside and isovitexin x″-*O*-xyloside from *Dracontium asperum* and a mixture of the two apigenin di-*C*-glycosides, schaftoside and isoschaftoside, from *Anthurium bellum*, *Philodendron eichleri* and *P. smithii*. Five new methylated flavone *C*-glycosides were characterized from *Asterostigma riedelianum*: 6,8-di-*C*-arabinosylapigenin 7,4′-dimethyl ether, 2″-*O*-glucosyl-6-*C*-arabinosylapigenin 7,4′-dimethyl ether, 2″-*O*-(caffeoyl) glucosyl-6-*C*-arabinosylapigenin 7,4′-dimethyl ether and the 7-monomethyl ethers of the mono-*C*-arabinosides. Data for these compounds are published elsewhere [17].

Flavones

Simple flavones (in 6% of the sample) are rare leaf constituents of the Araceae. They were found in six members of the tribe Arinae of the subfamily Aroideae. Luteolin and chrysoeriol were identified in *Arum italicum*, *A. maculatum*, *Biarum tenuifolium*, *Dracunculus canariensis* and *Typhonium giraldii* and chrysoeriol in *Arum italicum* subsp. *neglectum*. In *A. maculatum* luteolin and chrysoeriol 7-glucosides were characterized; while the former was reported by Koch and Steinegger, the latter was not detected by them [7]. Chrysoeriol was also detected in *Cryptocoryne wendtii* which is also in the Aroideae (subtribe Cryptocorynineae) and in *Scindapsus pictus* (Monsteroideae). In the present survey flavones were not detected in *Pistia stratiotes* but previously a luteolin 7-glycoside was reported from this taxon [6].

In addition, 4′-*O*-methylated flavones seem to be present in the family, at least in two *Anthurium* species (Pothoideae). Acacetin (4′-*O*-methylapigenin) has been positively identified in *Anthurium polyschistum*, but other as yet unidentified derivatives are also present.

Proanthocyanidins

Proanthocyanidins are frequent leaf constituents of the Araceae and were recorded in at least 35% of the species examined. However, these compounds may occur in as many as 45% of the sample, their presence being masked in acid-treated leaf extracts by cyanidin-based red pigments, which are found in the leaf tissue of some taxa. Proanthocyanidins were not detected in the Monsteroideae and Pistioideae and occurred in only one tribe (the Calleae, 1 species) of the Calloideae. In the remaining subfamilies they were common or frequent leaf components: Philodendroideae (66–85%), Lasioideae (50–63%), Colocasioideae (36–59%), Pothoideae (27%) and Aroideae (14–18%). Propelargonidin was found in only one species, *Rhektophyllum mirabile* in the subfamily Lasioideae; in all other cases procyanidin was present.

Phenolic sulphates

Flavonoid sulphates were uncommon in the family. They could only be identified in leaves of four species: vitexin and isovitexin 7-sulphates in *Philodendron ornatum* (Philodendroideae), a possible vitexin disulphate in *Culcasia saxatilis*, a vitexin 7-glucosidesulphate in an unnamed *Culcasia* species (Pothoideae) and a mixture of chrysoeriol galactosidesulphate and quercetin 3-sulphate in *Scindapsus pictus* (Monsteroideae). Dark to dark or dark to yellow (in UV and NH$_3$) negatively charged compounds were present in a small number of other taxa but the amounts were too small to allow their characterization (see Table 2).

Other types of phenolic sulphates are also probably present in the family. Compounds with the colour reactions of sulphated caffeic acid esters were detected in 20 % of the species surveyed. They were mainly present in the Monsteroideae (in 67 % of species) but were also fairly common in the Pothoideae (in 20 %) and Philodendroideae (in 23 %). Two compounds were obtained from *Anthurium hookeri* and their characterization as caffeic acid ester sulphates confirmed by spectral and hydrolytic procedures. Their R_fs and electrophoretic mobilities were closely similar to caffeoyl glucose-sulphates recorded in *Paspalum* (Gramineae) [18] and *Adiantum* (Filicales) [19], but the nature of the ester moiety was not further characterized.

A second caffeic acid derivative, which appeared as a slow moving anionic pale blue to intense blue spot (in UV and with NH_3) on electrophoresis, was also fairly common in leaf extracts of the Araceae. Its anionic mobility is due to the presence of acidic group(s) and not to sulphation. It is characteristically present in the Colocasioideae (in 80 % of taxa surveyed), frequent in the Lasioideae (in 38 %) and the Pothoideae (in 20 %). Neither this compound nor the caffeic ester sulphates described above were found at all in the Calloideae. Both caffeic acid derivatives appear to be restricted to certain groups within the family and thus may be of some taxonomic interest in the family.

DISCUSSION

A summary of the present results (Table 4) clearly establishes that the Araceae have a simple flavonoid profile in terms of both their anthocyanin pigments and their main classes of leaf constituents. Four flavonoid types are represented in the leaves: flavone *C*-glycosides, flavonols, flavones and proanthocyanidins. In contrast to the earlier finding that flavonols were the major constituents [4], it is now clear that flavone *C*-glycosides are in fact the most characteristic leaf components in this family. However, in the temperate tribe Symplocarpeae of subfamily Calloideae, they are replaced by complex mixtures of flavonol glycosides. Although flavonols are also present in some tropical species, they always co-occur with flavone *C*-glycosides, except in the case of *Scindapsus pictus* and *Stylochiton* species. A comparison of the present data with that for other monocot families previously surveyed (Table 6) reveals that the Araceae is also unusual in the paucity of species which produce simple flavones (luteolin, apigenin or chrysoeriol) and the apparent absence of species with more complex methylated flavones (e.g. tricin) and 6- or 8-hydroxylation. Indeed the predominance of flavone *C*-glycosides, often considered to be primitively retained characters [20], and the presence of proanthocyanidins in over one third (35–45 %) of the species surveyed suggests that the family is chemically more primitive than most other monocot groups. However, the diversity of *C*-glycosylation and the occurrence of methylated flavone *C*-glycosides in some species may indicate a different form of chemical advancement in this family.

In the absence of a good fossil record the phylogeny of the Araceae is uncertain and is a subject of some dispute among taxonomists. Thus, Engler [2] treated the aroids as derivatives of the Palmae via the Cyclanthaceae, whilst Wettstein [21] suggested that they were more advanced than the orchids and were probably derived from Helobiae–Liliiflorae stocks. Bessey [22] considered the Araceae and Palmae as parallel or divergent lines from Liliaceous ancestors. Takhtajan [23] and Cronquist [24] also associate the Araceae with the Palmae and Cyclanthaceae, while Hutchinson [25] groups them with his Liliales, Alstroemeriales and Typhales, suggesting that they arose from stock of the tribe Aspidistreae of the Liliaceae.

The present flavonoid evidence does not support the view that the Araceae is derived from Liliaceous stock, since flavone *C*-glycosides, the characteristic constituents of the aroids, are rarely found in present day Lilliaceae [26] and not at all in the tribe Aspidistreae. The only other monocot families which do accumulate glycosylflavones as major leaf components are the Gramineae, Palmae, Cyperaceae, Commelinaceae and Orchidaceae (see Table 6). However, in the grasses, palms and sedges the leaf flavonoids are more complex than in the aroids and it is only in the Orchidaceae and Commelinaceae that there are simple flavonoid patterns comparable with those of the Araceae. However, the anthocyanin patterns in both the Orchidaceae and Commelinaceae [33] are more complex

Table 4. The distribution of flavonoids at subfamily level in the Araceae

Subfamily*	Flavone *C*-glycosides	Flavonols	Flavones	Proanthocyanidins
Pothoideae (30)	+ + +	+	–	+ +
Monsteroideae (12)	+ +	(+)	(+)	–
Calloideae (4)	+ +	+ + +	–	+ +
Lasioideae (8)	+ + +	–	–	+ + +
Philodendroideae (39)	+ + +	+ +	–	+ + +
Colocasioideae (22)	+ + +	+ + +	–	+ + (or + + +)
Aroideae (28)	+ + +	+	+ +	+
Pistioideae (1)	+ + +	–	+ + +†	–

* Classification according to Engler [2], modified by Bogner [1]. Number of species surveyed in parentheses.

† Not found in present survey but recorded previously [6].

(+) in < 10 % of species; + in 10–25 % of species; + + in 25–50 % of species; + + + in > 50 % of species.

than (and different from) those in the Araceae, so that there is little chemical evidence linking the Araceae with either of these two groups.

No one subfamily of the Araceae is clearly distinguished by its flavonoid profile, although a number of trends may be seen (Table 4). Thus in species of the Lasioideae only flavone *C*-glycosides and proanthocyanidins were identified, while in the Monsteroideae flavonoids were apparently absent from half the species surveyed. The Pothoideae, Philodendroideae, Colocasioideae and Aroideae gave similar glycoflavone, flavonol, proanthocyanidin patterns but the Aroideae are distinguished by the presence of flavones in a number of species. The Calloideae, on the other hand, are unusual in the predominance of flavonol glycosides in one tribe, the Symplocarpeae (3 genera) and the presence of glycoflavones in the other, the Calleae (1 species).

However, a comparison of the occurrence of the four main groups of flavonoids at different taxonomic ranks reveals that the most significant patterns emerge at tribal level (see Table 5). Treatment at subfamily rank tends to obscure the fact that in certain groups, e.g. subfamily Pothoideae, the relationships between the constituent tribes are considered on morphological grounds to be rather remote, and it is interesting that this view is supported by the present results. The chemical evidence also highlights certain areas of the family classification already considered possibly anomalous on other grounds.

Though broader sampling of a number of tribes is necessary, some suggestive taxonomic indications are apparent:

1. The taxonomic heterogeneity of subfamily Pothoideae is confirmed by the flavonoid results, with tribe Anthurieae standing out as particularly distinct. Somewhat surprisingly, however, tribe Acoreae shows no differentiation from the Culcasieae or Zamioculcasieae, to neither of which it appears to be closely related on other grounds. Indeed there are strong arguments for placing *Acorus* in its own subfamily.
2. The two tribes within subfamily Calloideae show rather distinct flavonoid profiles, confirming their taxonomic separation.
3. The results of both anthocyanin pigment and leaf flavonoid surveys confirm the previously suspected closer relationship of *Anchomanes* to tribe Nephthytideae rather than to Pythonieae, where it was placed by Engler. The transfer of this genus to the Nephthytideae is strongly indicated also by cytological, geographical and morphological data. (Tribe Nephthytideae has been treated as including *Anchomanes* in Table 5.)
4. Though only one species of the tribe was studied, it is interesting that the Dieffenbachieae appear to have a rather different flavonoid profile from other tribes in subfamily Philodendroideae, and this supports the views of some, based on cytological and morphological evidence, that the relationships of this tribe require closer examination.
5. The very isolated taxonomic position of tribe Stylochitoneae within subfamily Aroideae is supported by the flavonoid results, which are curiously similar to those for tribe Symplocarpeae in subfamily Calloideae.
6. Tribe Areae in subfamily Aroideae also emerges as rather distinct chemically and appears to be unique in the family in having a high incidence of flavones.
7. In a previous study of the flavonoid pattern of *Gymnostachys*, Williams *et al.* [5] demonstrated the presence of a single unusual flavonol glycoside (kaempferol 3-sophoroside-7-rhamnoside). This profile contrasts markedly with that of *Acorus* presented here. According to the classic Englerian classification, *Acorus* and *Gymnostachys* together make up the tribe Acoreae, but the floral anatomy survey of Eyde *et al.* [34] and studies by P. B. Tomlinson (personal communication) strongly suggest that these two taxa are unrelated. This viewpoint is further supported by the flavonoid evidence.

Finally, a word about the relationship between flavonoid chemistry and geography is in order. In the Araceae, unlike the Orchidaceae [11] and Cyperaceae [28], there is no clear correlation between the flavonoid data and plant geography in that similar aglycone patterns were found in both Old and New World members. However, two of the most chemically heterogeneous groups, the large genera *Anthurium* and *Philodendron* (Tables 1–3) are found in tropical America. Here the flavonoid evidence reflects morphological and cytological diversity but without supporting any existing subgeneric groupings. In contrast, in a number of other New World genera: *Heteropsis*, *Monstera*, *Stenospermation* and *Dieffenbachia*, and two Old World genera: *Pothos* and *Epipremnum*, no flavonoid constituents were detected. Perhaps the most chemically homogeneous group in the family is the subtribe Arinae of the subfamily Aroideae. Here six of the eight members examined: *Arum maculatum*, *A. italicum*, *A. italicum* subsp. *neglectum*, *Biarum tenuifolium*, *Dracunculus canariensis* and *Typhonium giraldii*, gave almost identical leaf flavonoid glycoside patterns, a result which supports the close morphological relationships of the genera of this subtribe.

EXPERIMENTAL

Plant material. Verified plant material was received from various sources; see Tables 1 and 2 for details.

Anthocyanin identifications. Anthocyanins were surveyed by 1-D PC in the four standard solvents [35] against cyanidin 3-rutinoside as marker. In the majority of taxa and where sufficient pigment was available, the anthocyanins were separated and purified by PPC and identified by co-chromatography with markers, by spectral measurements and by detection of the appropriate anthocyanidin and sugars on acid hydrolysis. In the case of cyanidin 3-gentiobioside, identity was further confirmed by H_2O_2 oxidation and direct chromatographic comparison of the gentiobiose formed with authentic disaccharide.

Identification of leaf flavonoids. Flavonoid aglycones were identified in acid hydrolyzed leaf extracts using standard procedures and in comparison with authentic markers. Direct 80% methanolic extracts of leaf tissue were chromatographed two dimensionally in BAW and 15% HOAc. Known glycosides, isolated and purified by standard procedures were characterized on the basis of R_f, UV spectral analysis, acid hydrolysis to aglycone and sugar, and where possible by direct comparison with authentic markers. Flavonoid sulphates were detected by paper electrophoresis of direct leaf MeOH extracts at pH 2.2 (HOAc–HCO_2H buffer) for 2 hr at 400 V. Flavone *C*-glycosides were confirmed by 4 hr acid hydrolysis, extraction into amyl alcohol and PC against authentic markers in BAW, H_2O and CAW.

Identification of kaempferol 3-(6-arabinosylgalactoside) from Lysichiton camtschatcense. The glycoside was isolated from an 80% methanolic leaf extract by PPC in 15% HOAc, BAW and BEW. R_f data are given in Table 6. Acid hydrolysis with 2 N HCl

Table 5. The distribution of flavonoids at tribal level in the Araceae

Subfamily, tribe†	Flavone *C*-glycosides	Flavonols	Flavones	Proanthocyanidins
Pothoideae				
Pothoeae (1)	−	−	−	−
Heteropsidae (1)	−	−	−	−
Anthurieae (21)	+ + +	+	−	+ +
Culcasieae (2)	+ + +	−	−	−
Zamioculcaseae (4)	+ + +	−	−	−
Acoreae (1)	+ + +	−	−	−
Monsteroideae				
Monstereae (10)	+ +	(+)	(+)	−
Spathiphylleae (2)	+ +	−	−	−
Calloideae				
Symplocarpeae (3)	−	+ + +	−	−
Calleae (1)	+ + +	−	−	+ + +
Lasiodeae				
Lasieae (3)	+ + +	−	−	+ + (?)
* Pythonieae (1)	+ + +	−	−	−
* Nephthytideae (4)	+ + +	−	−	+ + +
Montrichardieae		Not sampled		
Philodendroideae				
Philodendreae (32)	+ + +	+ +	−	+ + +
Anubiadeae (1)	+ + +	−	−	+ + +
Aglaonemateae (2)	+ + +	−	−	+ + +
Dieffenbachieae (1)	−	−	−	−
Zantedeschieae (1)	+ + +	−	−	−
Typhonodoreae (1)	+ + +	−	−	+ + +
Peltandreae (1)	+ + +	+ + +	−	+ + +
Colocasioideae				
Colocasieae (18)	+ + +	+ + +	−	+ + (or + + +)
Syngonieae (2)	+ + +	−	−	+ +
Ariopsideae		Not sampled		
Aroideae				
Stylochitoneae (4)	−	+ + +	−	+
Arophyteae (7)	+ + +	−	−	+ +
Asterostigmateae (2)	+ + +	−	−	−
Protareae (1)	+ + +	−	−	−
Callopsideae (1)	+ + +	−	−	−
Zomicarpeae		Not sampled		
Areae (13)	+ + +	−	+ + +	−
Pistioideae				
Pistieae (1)	+ + +	−	+ + +‡	−

* For the purposes of this table, the genus *Anchomanes* has been transferred from the Pythonieae to the Nephthytideae (see Discussion).

† Classification according to Engler [2] modified by Bogner [1]. Number of species surveyed in parentheses.

‡ Not found in present survey but recorded previously [6].

(+) in < 10% of species; + in 10–25% of species; + + in 25–50% of species; + + + in > 50% of species.

for 30 min gave kaempferol, arabinose and galactose. λ_{max} for the glycoside: MeOH 270, 356; +NaOAc 276, 380; +H_3BO_3 273, 356; +alk 278, 408; +$AlCl_3$ 276, 356, 400; +$AlCl_3$/HCl 276, 356, 400. The positive NaOAc shift and dark to yellow colour (in UV + NH_3) of the glycoside indicates that both sugars are attached at the 3-position. H_2O_2 oxidation of the glycoside gave a disaccharide which co-chromatographed in BAW, BEW, phenol, BBPW and co-electrophoresed in borate buffer pH 8.8 for 3 hr with the disaccharide released by H_2O_2 oxidation of authentic quercetin 3-*O*-(6-*O*-L-arabinopyranosyl)-β-D-galactopyranoside isolated from leaves of *Hydrocotyle vulgaris* [16].

The identification of kaempferol 3-xylosylgalactoside from Lysichiton camtschatcense. The glycoside was isolated and purified as above and R_f data are given in Table 6. Acid hydrolysis gave kaempferol, xylose and galactose. λ_{max} for the glycoside: MeOH 269, 355; +NaOAc 276, 368; +H_3BO_3 269,

Table 6. A comparison of the leaf flavonoids of the Araceae with those of some other monocot groups

Order or family	Flavone C-glycosides	Flavonols	Flavones (Lu, Ap or Chrys.)	Proantho-cyanidins	Tricin	6-Hydroxy-flavonoids	Flavonoid sulphates	Mangiferin	Reference
Araceae	+++	++	(+)	++	–	–	(+)	–	—
Bromeliaceae	+	++	+	–	–	+	–	–	[27]
Commelinaceae	+++	+	+	nd	(+)	(+)	–	(+)	*
Cyperaceae	++	+	+	++	+	+	(+)	–	[28]
Fluviales	++	(+)	+	(+)	–	–	+	–	[29]
Gramineae	+++	(+)	+	(+)	+++	–	+	–	[18]
Iridaceae	++	+	nd	+	+	–	nd	+	[4†]
Juncaceae	(+)	(+)	+++	+	–	–	+	–	[30]
Liliaceae	(+)	+	++	+	(+)	–	(+)	(+)	[26]
Orchidaceae	++	++	(+)	(+)	(+)	+	(+)	–	[11]
Restionaceae	+	+++	+	+++	–	+‡	(+)	–	[12]
Palmae	+++	+	+	+++	++	–	+++	–	[31]
Zingiberales	+	++	+	+++	–	–	(+)	–	[32]

* Del Pero de Martinez, M. A., unpublished data.

† Harborne, J. B., unpublished data.

‡ 8-Hydroxylation in the case of the Restionaceae.

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

355; +alk 278, 410; +$AlCl_3$ 276, 305, 345, 412; +$AlCl_3$/HCl 276, 305, 345, 412. The positive NaOAc shift and the dark to yellow colour (in UV + NH_3) of the glycoside indicated that both sugars are attached at the 3-position. Both the glycoside and authentic kaempferol xylosylglucoside remained unchanged after 4 hr with β-glucosidase at pH 5 37°, and these two glycosides co-chromatographed on PC in BAW, BEW, PhOH, 15% HOAc and H_2O. Although an authentic disaccharide was not available it seems highly probable that it is a xylosylgalactoside.

Partial identification of quercetin and kaempferol 3-galactosylglucosides (or glucosylgalactosides) from Orontium aquaticum. The glycosides were isolated as above and R_f data are given in Table 6. Acid hydrolysis gave galactose, glucoside and quercetin and kaempferol, respectively. λ_{max} for quercetin 3-galactosylglucoside: MeOH 257, 267', 358; +NaOAc 266, 272', 379; +H_3BO_3 262, 376. λ_{max} for kaempferol 3-galactosylglucoside: MeOH 266, 349; +NaOAc 272, 370, +H_3BO_3 266, 350. The positive NaOAc shifts and the dark to yellow colour (in UV + NH_3) of the glycosides indicate the sugars are attached at the 3-position in both glycosides. R_f data suggested that two sugars were present in each glycoside but there was not sufficient material in either case to determine the order of attachment of the glucose and galactose to the aglycone.

Flavonol glycosides from Symplocarpus foetidus. Two quercetin and two kaempferol glycosides which all gave galactose and glucose on acid hydrolysis were isolated as above. R_f data are given in Table 6. One quercetin and one kaempferol glycoside have R_fs similar to the corresponding quercetin and kaempferol 3-galactosylglucosides isolated from *Orontium aquaticum*. λ_{max} quercetin glycoside: MeOH 255, 267', 354; +NaOAc 266, 376; +H_3BO_3 261, 372. λ_{max} kaempferol glycoside: MeOH 266, 335; +NaOAc 273, 360; +H_3BO_3 266, 350. The positive NaOAc shifts suggest that the sugars are at the 3-position in both these glycosides. The small amount of plant material available made it impossible to purify the other quercetin and kaempferol glycosides sufficiently to allow their characterization but their R_f values suggest acylation or extra glycosylation.

Vitexin O*-glucoside and isovitexin* O*-xyloside from* Dracontium asperum. Glycosides were isolated and purified as above. Acid hydrolysis (40 min) gave glucose and xylose, respectively and a mixture of vitexin and isovitexin from both glycosides. Partial acid hydrolysis gave vitexin and isovitexin, respectively as the first product. Spectral data λ_{max} vitexin *O*-glucoside: MeOH 272, 336; +NaOAc 280, 383; +H_3BO_3 273, 336. λ_{max} isovitexin *O*-xyloside: MeOH 272, 335, +NaOAc 280, 378; +H_3BO_3 272, 335. Positive NaOAc shifts in both cases and

Table 7. R_f (× 100) data for new and unusual flavonoid glycosides and sulphates found in the Araceae*

Flavonoids	BAW	BEW	Solvents Phenol	15% HOAc	1% HCl
Quercetin					
3-(6-arabinosylgalactoside)†	41	49	34	47	20
3-galactosylglucoside‡	44	37	45	59	—
3-rutinoside	42	44	45	51	—
3-galactosylglucoside‖	46	43	41	49	—
3-galactosylglucoside possible acylated derivative‖	27	21	34	66	—
Kaempferol					
3-(6-arabinosylgalactoside)†	61	71	65	52	—
3-xylosylgalactoside†	59	71	66	64	—
3-xylosylglucoside	61	74	66	65	—
3-galactosylglucoside‡	50	51	71	61	—
3-galactosylglucoside‖	51	56	59	57	—
3-galactosylglucoside possible acylated derivative‖	25	22	51	76	—
Isorhamnetin					
3-galactosylglucoside‡	58	62	75	49	—
Vitexin	38	46	61	22	—
x''-*O*-glucoside§	30	48	63	74	—
7-sulphate¶	19	31	18	35	—
7-sulphate[x]	15	36	65	71	—
7-glucosidesulphate**	04	11	03	82	—
Isovitexin	63	57	58	46	—
x''-*O*-xyloside§	43	58	63	70	—
7-sulphate¶	34	48	34	60	—

* Some markers are given for comparison.

† Isolated from *Lysichiton camtschatcense*.

‡ Isolated from *Orontium aquaticum*.

§ Isolated from *Dracontium asperum*.

‖ Isolated from *Symplocarpus foetidus*.

¶ Isolated from *Philodendron ornatum*.

** Isolated from *Culcasia* sp.

[x] Isolated from *Culcasia saxatilis*; this compound probably has a second sulphate attached to one of the sugar hydroxyls.

the dark to yellow colour (in UV + NH_3) of the glycosides suggest that the *O*-sugar is attached to the *C*-sugar. R_f data for both glycosides are given in Table 6.

Flavonoid sulphate identifications. Flavonoid sulphates were isolated from 80 % methanolic leaf extracts by electrophoresis on 3MM paper at pH 2.2 (as above). Flavone *C*-glycosidesulphates were characterized by R_f, spectral data, 40 min and controlled acid hydrolysis to give the parent *C*-glycoside, *O*-sugar and HSO_4^- ion (detected by TLC, solvent 20 % 0.1 M HCl in EtOH, sprayed with sodium cobaltous hexanitrite). Chrysoeriol galactosidesulphate from *Scindapsus pictus* was tentatively identified as such from R_f data and acid hydrolysis, which gave chrysoeriol (co-chromatography in BAW, forestal, 50 % HOAc and CAW), galactose and HSO_4^-. Quercetin 3-sulphate from the same plant gave quercetin and sulphate on acid hydrolysis and showed the same electrophoretic mobility as an authentic marker. R_f data for flavonoid sulphates are given in Table 6. Electrophoretic mobilities compared with quercetin 3-sulphate as 1 are: vitexin 7-SO_4 (*Philodendron ornatum*), 0.75; vitexin 7-SO_4 (*Culcasia saxatilis*), 1.4; isovitexin 7-SO_4, 1.18; vitexin 7-glucoside SO_4, 3.6; chrysoeriol galactoside SO_4, 0.53. It was not possible to fully characterize the vitexin sulphates from the *Culcasia* species but the R_f data and electrophoretic mobilites suggest there may be two sulphate groups present in these compounds.

Caffeic acid derivatives. Sulphated caffeic acid esters were detected regularly (see Table 2) in Araceae as highly mobile anionic components on electrophoresis at pH 2.2 of direct leaf extracts, which had the typical colour reactions on paper of caffeic derivatives. Two components were isolated by electrophoresis from leaf extracts of *Anthurium hookeri* and studied in more detail. They had R_f values of 0.29 and 0.36 in BAW, 0.16 and 0.23 in BEW, and 0.78 and 0.87 in 15 % HOAc. Mobilities relative to quercetin 3-sulphate were 1.6 and 1.9. Spectral properties were identical to those of chlorogenic acid. On acid hydrolysis, they yielded caffeic acid but the ester moiety was not detected. Their R_f and electrophoretic properties are closely similar to those of a caffeoylglucose sulphate previously reported in *Paspalum* [18].

A novel phenolic component, which appeared pale purple in UV light changing to intense light blue in the presence of NH_3 was detected regularly in leaf extracts on electrophoresis (see Table 2). It was isolated from *Alocasia odorata*. It had a low mobility and was unchanged on acid treatment, so that it was not sulphated. R_f values were 0.91 in BAW, 0.27 in BEW, 0.91 in H_2O and 0.79 in 15 % HOAc. It had λ_{max} 225, 300 sh, 310 nm in EtOH and showed a bathochromic shift with alkali (357 nm). It appeared to give trace amounts of caffeic acid on acid hydrolysis, but was largely recovered unchanged on such treatment. It was not affected by β-glucosidase or β-glucuronidase. It appeared to be a caffeic acid derivative, substituted at the 3-hydroxyl, since it had similar colour properties to caffeic acid 3-glucoside.

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