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THE PRESENCE OF QUINONES IN THE GENUS *CYPERUS* AS AN AID TO CLASSIFICATION

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Key Word Index—*Cyperus*; Cyperaceae; quinonoids; roots; rhizomes; chemotaxonomy.

Abstract—The absence or presence and type of quinonoid constituents in the roots and rhizomes of the genus *Cyperus* have proved consistent with the accepted divisions within this genus but not with the arrangement within these divisions.

INTRODUCTION

Cyperaceae, the sedges, are a large cosmopolitan family of monocotyledons comprising about 3700 species within 70 genera [1]. Although it contains over 1% of known classified plants, very few species have been chemically investigated. 36 genera and about 530 species are represented in Australia, the largest genera being *Cyperus* (112 species), *Fimbristylis* (82 species), *Schoenus* (67 species) and *Carex* (45 species). *Carex* which is one of the largest plant genera with about 1200 species, is adapted to temperate regions and is poorly represented in Australia, whereas *Cyperus* predominates in tropical areas and is particularly well represented in Queensland. Although this work is not restricted to *Cyperus*, major emphasis has been placed on that genus.

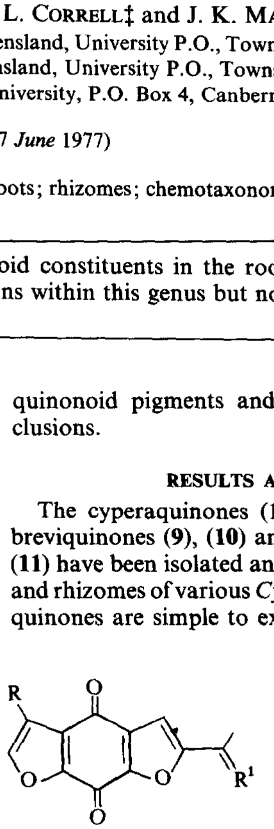
Classification of the family by classical methods is very difficult on account of the extreme reduction of the floral parts of many taxa. The limits of several genera (including *Cyperus*, *Fimbristylis* and *Scirpus*) are still debated by leading taxonomists, and there is no general agreement as to the best suprageneric classification of the family [2].

Two previous chemotaxonomic studies of sedges have been reported [3, 4] using the flavonoid pigments from the leaves. No striking correlations were revealed between chemistry and classification of taxa within the family but the results were useful in relating the Cyperaceae to certain other monocot families.

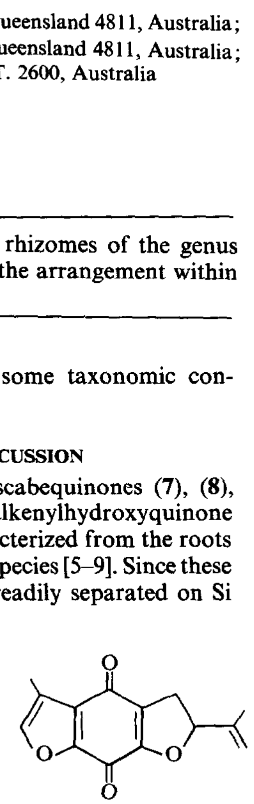
We have previously reported the isolation of quinones [5–8] from several species of *Cyperus* and during the course of our work we noticed many excellent correlations between the occurrence of certain quinonoid types in the roots and rhizomes of many species of the genus *Cyperus* and arrangement of these species within the genus. We now report a survey of over 100 species from 29 genera of Australian Cyperaceae for the presence of quinonoid pigments and draw some taxonomic conclusions.

RESULTS AND DISCUSSION

The cyperaquinones (**1**)–(**6**), scabequinones (**7**), (**8**), breviquinones (**9**), (**10**) and the alkenylhydroxyquinone (**11**) have been isolated and characterized from the roots and rhizomes of various *Cyperus* species [5–9]. Since these quinones are simple to extract, readily separated on Si



(**1**) R = Me, $R^1 = CH_2$
(**2**) R = CH_2OH, $R^1 = CH_2$
(**5**) R = H, $R^1 = CH_2$
(**6**) R = Me, $R^1 = O$



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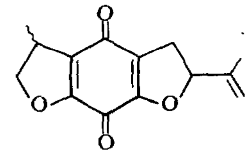

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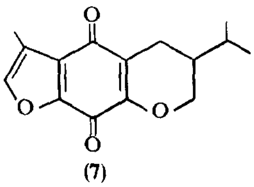
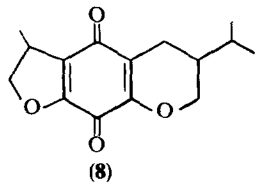


(**7**)



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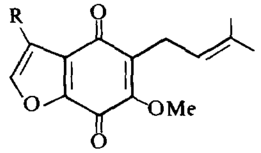
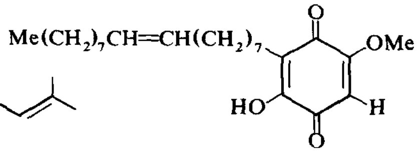


(**9**) R = Me
(**10**) R = CH_2OH



(**11**)

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Table 1. TLC properties of quinones isolated from *Cyperaceae*

Formula	Name	R_f on Si gel G C_6H_6	CH_2Cl_2	C_6H_6–EtOAc (4:1)	Colour on Si gel
1	Cyperaquinone	0.43	0.69	0.84	Magenta
2	Hydroxycyperaquinone	0.03	0.08	0.34	Magenta
3	Dihydrocyperaquinone	0.28	0.60	0.80	Orange
4	Tetrahydrocyperaquinones	0.16	0.49	0.72	Purple
5	Demethylcyperaquinone	0.35	0.62	0.81	Magenta
6	Conicaquinone	0.09	0.27	0.65	Deep Yellow
7	Scabequinone	0.21	0.59	0.69	Yellow
8	Dihydroscabequinone	0.12	0.46	0.59	Orange–red
9	Breviquinone	0.55	0.68	0.87	Orange–yellow
10	Hydroxybreviquinone	0.05	0.14	0.46	Orange–yellow
11	Hydroxydietrichequinone	0.09	0.38	0.59	Purple–brown

gel, and have characteristic colours, they are readily detected in plant material. The quinones determined in the survey are listed in Table 1 with their colour on Si gel and R_f properties in three solvents.

Over a hundred species from 29 genera were examined in this survey representing approximately a quarter of the species and three quarters of the genera in Australia. *Carex* is not well represented in North Queensland and only four species were examined. The distribution of quinones in the sedges examined is shown in Table 2. One occurrence in the genus *Fimbristylis* was noted but there was inadequate material for positive identification of the species or the quinones present. The concentration of quinones isolated from the roots and rhizomes varied greatly with the species ranging from 0.007% in *Cyperus compressus* to 1.6% in *Remirea maritima*. In many taxa no quinones were detected. A seasonal variation in quinone content of some species (e.g. *Cyperus haspan*) was noted, and it was also found that mature plants had a higher content than immature ones. Nevertheless, quinones could always be detected in the roots of those species previously known to contain them.

Of the 107 species studied *Remirea maritima* was the only one outside the subfamily Scirpoideae which contained quinones. This monospecific genus is placed in the Rhynchosporoideae by many authors [10, 11] on account of its single flowered spikelets. The spikelet of *Remirea* has been shown to be a reduced form of the *Cyperus* type of spikelet and consequently some authors, e.g. Kern [12], advocate its transfer to *Cyperus (sens. lat.)*. This transfer would eliminate this anomalous occurrence of quinones in the Rhynchosporoideae and is supported by the phytochemical data presented here.

As all but two of the other occurrences of quinones were in *Cyperus* this investigation has been concentrated on that genus. Table 2 includes the results of analyses of some 47 species of *Cyperus*. The distribution of the quinones within *Cyperus* was found to be in general agreement with the sections recognized by Kükenthal [11]. Twelve sections of the genus were represented by more than one species and only in the *Rotundi* were there quinone-positive and -negative species. The three species in this section are all rich in sesquiterpenes. In this work it was found that *C. stoloniferus* contained 1% α-cyperone and 1% selinenes [13] both of which have been isolated from *C. rotundus* and *C. corymbosus* var. *scariosus* [14]. The section Graciles was represented by six species, all of which lacked quinones.

Two of the four subgenera of Cyperus represented in this survey included some quinone-containing species. The two subgenera, *Pycreus* and *Kyllinga*, which have often been regarded as separate genera, lack quinones. Both taxa differ from all other *Cyperus* species by having lenticular nuts with an angle next to the rachilla of the spikelet. Clarke [15] placed *Pycreus* and *Kyllinga* next to each other, and this arrangement is consistent with our results.

The distribution of scabequinones ((**7**) and (**8**) in Table 2) is of particular interest. They occur only in the *Distantes (Eucyperus)* and *Strigosi (Mariscus)*, suggesting that these two sections are more closely related than indicated by Kükenthal's classification of the genus. The descriptions of these two sections are very similar and their separation is unnatural from both the morphological and phytochemical point of view.

Kükenthal's primary division of *Cyperus* based on the disarticulation of the spikelets places *Eucyperus*, *Pycreus* and *Juncellus* in one group and *Mariscus*, *Torulinum* and *Kyllinga* in the other. This division is difficult to use in practice for separating *Eucyperus* from *Mariscus*. This study suggests that the division is also an unnatural one. As discussed above, *Pycreus* and *Kyllinga* should not be widely separated. The sections *Distantes* and *Strigosi* are closely related and should not be widely separated as is done by Kükenthal. In fact the quinones occur with equal frequency on both sides of the division, suggesting that this classification is artificial.

It had been suggested [5] that dihydrocyperaquinone (**3**) is a precursor for the other cyperaquinones. It would follow that accumulation of this compound is a more primitive character than the accumulation of other members of the series. To date this compound has been found in *Cyperus alopecuroides*, *C. platystylis*, *C. alternifolius*, *C. stoloniferus* and *Remirea*. The scattered distribution of (**3**) is consistent with its being a primitive character. Bentham [10] commented on *C. platystylis* that its style is quite that of a *Fimbristylis*. This would concur with our hypothesis that this species is primitive. Bentham grouped *C. platystylis* and *C. alopecuroides* together and the fact that both contain dihydrocyperaquinone would lend phytochemical support to this classification.

C. dietricheae var. *brevibracteatus* and *C. dietricheae*

Table 2. The distribution of quinones in a sample of sedge taxa

Taxa	Presence of quinones†	Type and ratio of quinones‡
SUBFAMILY CYPEROIDEAE		
Bulbostylis barbata (Rottb) C. B. Clarke	–	
*Cyperus**		
Subgenus *Eucyperus*		
Section *Papyrus*		
C. papyrus L.	–	
Section *Exaltati*		
C. exaltatus Retz.	++	1
C. Alopecuroides Rottb.	++	3
Section *Brevifoliati*		
C. corymbosus var. *scariosus* (R. Br.) Kükenth	–	
Section *Proceri*		
C. pilosus Vahl.	++	1
Section *Rotundi*		
C. rotundus L.	–	
C. stoloniferus Retz.	+	1, 2 (1:1)
Section *Subquadranglares*		
C. zollingeri Steud.	–	
C. sphacelatus Rottb.	–	
Section *Distantes*		
C. distans L.	++	7, 8 (10:11)
C. eleusinoides Kunth	+	7
Section *Iriae*		
C. iria L.	–	
Section *Compressi*		
C. compressus L.	+	5
Section *Luzuloidei*		
C. eragrostis Lam.	++	1, 2 (2:1)
Section *Pseudanosporum*		
C. platystylis R. Br.	++	3 and others
Section *Vaginati*		
C. vaginatus subsp. *gymnocaulos* (Stendel) Kükenth	+++	1, 2 (10:1)
C. vaginatus R. Br.	+++	1, 2 (10:1)
C. alternifolius L.	+	3, 4 (1:1)
Section *Fusci*		
C. difformis L.	–	
Section *Haspani*		
C. haspan L.	+++	1, 2 (1:8)
Section *Graciles*		
C. trinervis var. *aquatilis* (R. Br.) Kükenth.	–	
C. enervis R. Br.	–	
C. gracilis R. Br.	–	
C. laevis R. Br.	–	
C. stradbrokensis Domin	–	
C. tenellus L.f.	–	
Subgenus *Pycreus*		
Section *Lancei*		
C. unioloides R. Br.	–	
Section *Albomarginati*		
C. albomarginatus (Nees) Mart. & Schrad.	–	
Section *Polystachyi*		
C. polystachyos Rottb.		
Section *Pumili*		
C. pumilus var. *nervulosus* Kükenth.	–	
C. pumilus L.	–	
Section *Sulcati*		
C. sanguinolentus Vahl.	–	
Subgenus *Mariscus*		
Section *Strigosi*		
C. scaber (R. Br.) Beck	+++	7, 8 (10:1)
Section *Subulati*		
C. dietricheae var. *brevibracteatus* (Domin) Kükenth.	++	9, 10 (5:1)
C. dietricheae Boeck.	++	11
C. subulatus R. Br.	++	1,2 (10:1)
Section *Thunbergiani*		
C. haematodes Endl.	–	
C. congestus Vahl	–	
Section *Pinnati*		
C. aff. dactylotes Benth.	++	11
C. fulvus R. Br.	++	11
C. rutilans (C. B. Clarke) Maiden & Betche	++	11
Section *Turgiduli*		
C. conicus (R. Br.) Boeck	++++	1, 2, 6, (20:4:1)
C. decompositus (R. Br.) F. Muell.	+++	11, 1, 2 (10:2:trace)
C. javanicus Houtt.	++	1, 2 (6:1)
Section *Aristati*		
C. aristatus Rottb.	+++	1, 5 (1:1)
Section *Umbellati*		
C. cyperoides (L.) O. Ktze	+++	1, 2 (6:1)
Subgenus *Kyllinga*		
Section *En-Kyllinga*		
C. brevifolius (Rottb.) Hassk.	–	
Section *Alati*		
C. kyllingia Endl.	–	
Eleocharis acuta R. Br.	–	
E. difformis S. T. Blake	–	
E. dulcis (Burm. f.) Trin. ex Henschel	–	
E. geniculata (L.) Roem. & Sch.	–	
E. gracilis R. Br.	–	
E. sphacelata R. Br.	–	
Fimbristylis acicularis R. Br.	–	
F. ferruginea Vahl	–	
F. monostachya Hassk.	–	
F. nuda Boeck.	–	
Fuirena ciliaris L.	–	
F. umbellata Rottb.	–	
Lipocarpha microcephela (R. Br.) Kunth	–	
Scirpus articulatus L.	++++	Not determined
S. inundatus (R. Br.) Spreng.	–	
S. littoralis Schrad.	–	
S. maritimus L.	–	
S. mucronatus L.	–	
S. nodosus Rottb.	–	
S. platycarpus S. T. Blake	–	
SUBFAMILY RHYNCHOSPOROIDEAE		
Arthrostylis aphylla R. Br.	–	
Baumea huttonii (T. Kirk) S. T. Blake	–	
Carpha nivicola F. Muell.	–	
Caustis flexuosa R. Br.	–	
Cladium filum (Labill.) R. Br.	–	
Cyathochaete avenacea (R. Br.) Benth.	–	
Evandra aristata R. Br.	–	
Exocarya scleroides (R. Muell.) Benth.	–	
Gahnia asperata (R. Br.) Spreng.	–	
G. sieberiana Kunth	–	

Table 2. The distribution of quinones in a sample of sedge taxa (*continued*)

Taxa	Presence of quinones†	Type and ratio of quinones‡
Hypolytrum latifolium L. C. Rich.	–	
Lepironia articulata (Retz.) Domin	–	
Mesmolaena tetragona (R. Br.) Benth.	–	
Oreobolus pumilo R. Br.	–	
Ptilanthelium deustum (R. Br.) Steud.	–	
Remirea maritima Aubl.	+ + + + +	1, 3, 4 (1:25:3)
Rhynchospora corymbosa (L.) Britton	–	
R. heterochaete S. T. Blake	–	
R. leae C. B. Clarke	–	
R. rubra (L.) Makino	–	
R. tenuifolia Benth.	–	
Schoenus apogon Roem. & Sch.	–	
S. brachyphyllus F. Muell.	–	
S. deformis (R. Br.)	–	
S. kennyi (F. M. Bailey) S. T. Blake	–	
S. nitens (R. Br.) Poir.	–	
S. sparteus R. Br.	–	
Scleria brownii Kunth	–	
S. levis Retz.	–	
S. sphacelata F. Muell.	–	
Tetraria capillaris (F. Muell.) J. M. Black	–	
SUBFAMILY CARICOIDEAE		
Carex appressa R. Br.	–	
C. brunnea Thunb.	–	
C. gaudichaudiana Kunth	–	
C. neurochlamys F. Muell.	–	
Uncinia tenella R. Br.	–	

* The classification follows that of Kükenthal in Das Planzenreich.

† Indicates that no quinones were detected, + indicates quinones at the concentration of less than 0.001%, ranging up to + + + + + indicating a concentration of more than 1% of dried roots.

‡ The numbers in this column correspond to the compounds shown in Table 1. The numbers in parentheses indicate the ratios of the amounts of quinones present.

are classified as a single species and placed, together with *C. subulatus*, in the section *Subulati*, next to the section *Stringosi* which contains *C. scaber*. The different classes of quinones (**9**) and (**11**) found in *C. deitricheae* var. *brevibracteatus* and *C. dietricheae* indicate that they are distinct species (phytochemical results place *C. dietricheae* nearer to the *Pinnati*). The relationship of *C. scaber* and *C. deitricheae* var. *brevibracteatus* is found to be closer, by phytochemical methods, than that between the latter and *C. subulatus*. This again suggests that Kükenthal's classification is unsatisfactory.

Some species of *Cyperus* are extremely variable morphologically, e.g. *C. scaber*, *C. distans* and *C. compressus*, but this variation does not appear to affect the type or the relative amounts of the quinones present. The type and proportions of the quinones conversely may be of use in defining specific limits. Use of this may be made in deciding whether *C. vaginatus* subsp. *gymnocaulos* should be maintained as a separate species or as a subspecies of *C. vaginatus*. Kükenthal considered it to be a subspecies but Blake [16] later published a table listing differences between the two species adding, however, that some South Australian specimens were intermediate between the two. The quinones of both taxa are qualitatively identical and quantitatively very similar and on this basis there would appear no ground for maintaining *C. vaginatus* subsp. *gymnocaulos* as a separate species.

On the basis of this study it is considered that the distribution of quinones in the Cyperaceae and particularly in *Cyperus* will prove a useful character in arriving at a natural classification of the family. There are two major conclusions: first, the advocated transfer of the genus *Remirea* from the Rhynchosporoideae to the Scirpoideae is supported by our data; and second, the data presented in Table 2 are consistent with the accepted sections of the genus *Cyperus* but not with the arrangement within these sections.

EXPERIMENTAL

Wherever possible analyses were carried out on fresh material but in some cases herbarium material was used. If practical, replicate samples from different locations were included. Voucher specimens are housed in the Herbarium of the Department of Botany, James Cook University (JCT).

Testing root material for quinone content. Roots and rhizomes were washed and dried in the dark at room temp. The material was then finely sliced and 0.1–0.2 g immersed in $CHCl_3$ and allowed to stand 18 hr. After filtration the $CHCl_3$ extract was reduced to a vol. of *ca* 0.05 ml. The conc extract was then spotted on a TLC plate prepared from Keiselgel G (Merck) and run in one of the solvent systems shown in Table 1. If quinones were detected the remainder of the extract was run against pure samples of the quinones in the most appropriate solvent.

REFERENCES

1. Schultze-Motel, W. (1964) *Syllabus der Pflanzenfamilien* (Melchoir, H. ed.) Springer-Verlag, Berlin.
2. Kukkonen, I. (1967) *Aquilo. Ser. Botanica* **6**, 18.
3. Clifford, H. T. and Harborne, J. B. (1969) *Phytochemistry* **8**, 123.
4. Harborne, J. B. (1971) *Phytochemistry* **10**, 1569.
5. Allan, R. D., Correll, R. L. and Wells, R. J (1969) *Tetrahedron Letters* 4669.
6. Allan, R. D., Dunlop, R. W., Kendall, M. J., Wells, R. J. and MacLeod, J. K. (1975) *Tetrahedron Letters* 3.
7. Allan, R. D., Wells, R. J. and MacLeod, J. K. (1973) *Tetrahedron Letters* 7.
8. Dunlop, R. W., Wells, R. J. and MacLeod, J. K. in preparation.
9. MacLeod, J. K., Worth, B. R. and Wells, R. J (1972) *Tetrahedron Letters* 241.
10. Bentham, G. (1878) *Flora Australiensis* Vol. VII. L. Reeve and Co., London.
11. Kükenthal, G. (1909 and 1939) *Das Pflanzenreich* Heft 38 and 101. H. R. Engleman.
12. Kern, J. H. (1962) *Advan. Sci.* **19**, 141
13. Wells, R. J. unpublished results.
14. Allan, R. D. (1972) Ph.D. Thesis, James Cook University of North Queensland.
15. Clarke, C. B. (1908) *Kew Bull. Add. Ser.* **8**, 372.
16. Blake, S. T. (1940) *Proc. Roy. Soc.* **51**, 32.