# *Chapter 8*

#### **Phytochemical Diversity in Cyperaceae Members**

# **Abstract**

The phytochemistry of Cyperaceae members is generally restricted to the most common member, *Cyperus rotundus*, while there are 5687 species reported globally. A review of the phytochemistry of other Cyperaceae members revealed that only 180 species have been studied, and among the various Cyperaceae groups, *Cyperus* (97species), *Carex* (53 species) and *Scirpus* (19 species) are the major genera studied for their phytochemicals. Out of the 274 Cyperaceae members reported from south India, only 39 species have been investigated for their phytochemicals, and many of them are preliminary screening only. GC-MS studies on essential oils and LC-MS studies on solvent extracts are the most explored, while conventional phytochemical studies through extraction, chromatographic separation and spectroscopic characterization are comparatively less. In addition to volatile sesquiterpnoids, phenolic compounds are reported in plenty in the Cyperaceae species. Presence of characteristic compounds such as stilbenes and quinones warrants further studies on Cyperaceae members.

## **Introduction**

Traditionally, the phytochemical investigation of Cyperaceae members is restricted to the most widely used *Cyperus rotundus* and few related *Cyperus* species like *Cyperus scariosus,Cyperus conglomeratus, Cyperus esculentus, Cyperus distans, Cyperus articulatus* and *Cyperus longus,* which are being used in traditional medicinal systems in different parts of the world. Though several other Cyperaceae members are important region wise, they are least investigated with respect to their constitution or potential biological activities, and though the phytochemistry of *Cyperus rotundus* has been reviewed extensively, compilation of the phytochemistry of Cyperaceae members is rare (Taheri *et al.,* 2021).

The conventional analytical techniques, as well as the modern hyphenated analytical techniques have been used for the investigation of Cyperaceae phytochemistry. Harborne and team in their classical works employed traditional phytochemical techniques skilfully in elaborating the flavonoid profile of Cyperaceae members (Clifford and Harborne, 1969; Harborne, 1971; Harborne *et al.,* 1985). Noori *et al.* (2012) investigated the root flavonoids of 5 *Scirpus* species using 2-dimentional paper chromatography and thin layer chromatography. By employing the recent developments in phytochemical analytical techniques, Elshamy *et al*. (2020) performed a comprehensive metabolite profiling of *Cyperus conglomeratus* using UPLC-qTOF-MS, and 70 compounds including organic acids, phenolic acids, cinnamic acid derivatives, flavonoids, stilbenes, aurones, quinones, terpenes and steroids were identified by comparing retention times and MS data, through accurate mass, isotopic distribution, and fragmentation pattern in both negative and positive ionization modes. Though widely distributed with remarkable traditional uses, the Indian Cyperaceae plants are generally least investigated (Rajak and Ghosh, 2022).

Phytochemistry of Cyperaceae members can be broadly divided into proximate composition reporting mainly the primary metabolites, volatile composition and nonvolatile composition. Proximate analysis is used to estimate the relative amounts of protein, lipid, water, ash, carbohydrate *etc* in any sample, and is the first and foremost step to determine the identity and to assess the quality of plant material. Most of the Cyperaceae members are aromatic and the volatile chemicals have significance, while the characteristic phenolic, terpene and nitrogenous compounds are of non-volatile, and extractable with organic solvents.

#### **Proximate analysis of Cyperaceae members**

Geophytes, plants with underground storage organs, are important forage for animals, and the proximate analysis of the arial parts of geophytes has relevance with respect to the nutritional aspects of the forage plants (Al-Rowaily *et al.,* 2019; Mashaly *et al*., 2007). Cyperaceae plants that grow naturally in sandy habitats with low content of water has high dry matter content, usually around 90%. The less moisture content (generally less than 10%) makes them more stable for storage. The ash content is around 10% for *Cyperus capitatus*, while the crude fiber content is around 12% for *Cyperus conglomeratus*. The total protein content is considered as an indicator of the nutritional value and is relatively high ( $>10\%$ ) for Cyperaceae tubers. The dry matter of forage crops contains about 50-80% carbohydrates, and the energy level for *Cyperus capitatus* was 311.62 kcal 100 g<sup>-1</sup>.

Although fats are a concentrated source of energy, for Cyperaceae forage the fat content is significantly less, around 3%. However, few species such as *Cyperus esculentus* are reputed as rich in fatty acids. *Cyperus esculentus* tubers, commonly known as Chufa tubers contain high amount of dietary fiberthat consists of insoluble carbohydrates, mainly cellulose and lignin. Chufa is potentially a commercial source of higholeic acid vegetable oil and highcarbohydrate tuber cakes. The proximate analyses reveal fats (30.2%), starch (35.0%), protein (12.0%), ash 1.2 %), dietary fibre (9.8%) and sucrose 11.8% in *Cyperus esculentus* tubers (Coşkuner *et al.,* 2002). Mineral composition of forage has essential physiological roles in animals, in maintaining the livestock health, and Cyperaceae forage is reported to have both macro (K, Ca, Mg, and Na) and micro elements (Fe, Mn, Zn, and Cu), and have comparatively higher contents of Na, Fe and Mn.

## **Comparative nutritional analysis of** *Cyperus rotundus* **and** *Cyperus esculentus*

The nutritional analysis of Cyperaceae members needs much attention since several Cyperaceae species are used as food from ancient times onwards. Studies revealed that, among the various Cyperaceae members, *Cyperus rotundus* and *Cyperus esculentus* were highly nutritional**.** Musa *et al*. (2020) had done a comparative proximate analysis of *Cyperus rotundus* and *Cyperus esculentus. Cyperus rotundus* had a higher moisture content than *Cyperus esculentus* which could mean that the *Cyperus esculentus* variety can be stored longer than the *Cyperus rotundus*variety. Total ash content is a rough indicator of the mineral content of a food sample. *Cyperus rotundus* had higher ash content than *Cyperus esculentus* suggesting higher mineral content than *Cyperus esculentus*. The presence of zinc, copper, cobalt, calcium and phosphorus in both species suggest that regular consumption could help mitigate the diseases resulting from these mineral deficiencies. *Cyperus rotundus* and *Cyperus esculentus* consist of some trace elements also. Ekeanyanwu and Ononogbu (2010) reported that the lipid found in *Cyperus rotundus* and *Cyperus esculentus* is edible. Carbohydrate is abundant in both the species. The free carbohydrates D-saccharose, D-glucose, D-mannitol and D-fructose were determined in *Cyperus esculents*. The total content of fructans was determined by the spectrophotometric method at13.5% and in tubers the fructans content was 8.8% (Marchyshyn *et al*., 2021). Adejuyitan (2011) also reported relatively low protein content for both *Cyperus rotundus*

and *Cyperus esculentus*. The low protein content suggests that although both the species have rich energy content and high satiety values, they cannot be used as complete or whole diet because of the low protein content.

# **Phytochemicals reported from Cyperaceae members**

Literature review on the phytochemicals reported from Cyperaceae members revealed that out of the 5687 Cyperaceae members, only 180 species have been investigated for the constituents (**Table 1).** Out of the 274 Cyperaceae members reported from south India, only 39 species have been investigated for their phytochemicals, and many of them are preliminary screening only. Only the major components of the essential oils are included in the table. In addition to *Cyperus* (97 species), the major genera investigated for the phytochemicals are *Carex* (53 species) and *Scirpus* (19 species). Out of the 274 Cyperaceae members reported from south India, only 39 species have been investigated for their phytochemicals, of which *Cyperus* is the major genus with 31 species, followed by *Carex* (3 species), *Kyllinga* (3 species), *Rhynchospora* (1 species) and *Scleria* (1 species). Volatile chemical studies through GC-MS and LC-MS studies of solvent extracts are the most explored, while the number of species investigated through conventional phytochemical steps such extraction, chromatographic separation and spectroscopic characterization are much less.







































































## **Phenolic compounds reported from Cyperaceae members**

Literature review revealed that, in addition to the volatile chemicals, the Cyperaceae have been investigated generally for their polyphenols such as phenolic acids, benzoic acids, cinnamic acids, flavonoids, stilbenes, aurones and quinones (Clifford and Harborne, 1969; Harborne, 1971; Williams, and Harborne, 1977; Harborne *et al.,* 1982; Harborne *et al*., 1985; El-Habashy *et al.,* 1989). The availability of standard polyphenol compounds, and the established extraction and analytical protocols make polyphenols an easy target for phytochemical analysis. Investigation of polyphenolics has significance in

chemotaxonomy, nutritional, medicinal and ecological aspects. Plants having different types of polyphenolic compounds have been used as potential therapeutics due to the antioxidative, anti-cancerous and anti-inflammatory properties associated with the polyphenolics (Gil *et al*., 2000).

## **Flavonoids**

Flavonoids are the most widely distributed phenolic compounds in Cyperaceae members (**Table 1, Figure 1**). The two-dimensional chromatographic analysis by Harborne (1971) revealed the presence of five pharmacologically important flavonoids such as kaempferol, quercetin, glycoflavone, luteolin and tricin in the leaves of different members of the tribe *Scirpae*, *Rhynchosporae* and *Cypereae*. El-Habashy *et al.* (1989) investigated 20 *Cyperus* and four *Pycreus* species for their flavonoids and glycosides and the data was used for chemotaxonomy. Recent phytochemical investigation using HPLC revealed the presence of gallic acid, phloroglucinol, catechin, caffeic acid, coumaric acid, ferulic acid, rosmarinic acid, quercetin and biochanin in different *Carex* species (Rajak and Ghosh, **2022**). The coumarin remirol and the quinones cyperaquinone and scabequinone were identified as the antifeedant compounds in the stem of *Cyperus nipponicus* and *Cyperus distans* (Morimoto *et al.,* 1999).



**Figure 1.** Major flavonoids reported from *Cyperaceae* species. **A**- Luteolin, **B**- Tricin, **C**-Aureusidin, **D**- Apigenin, **E**- Quercetin and **F**- Kaempferol

Gamal *et al.* (2015) reviewed the phenolics in *Cyperus* species. Among the different flavonoids, luteolin is present in around 120 *Cyperus* species, while luteolin derivatives such as glycosides and methyl ethers were also abundant in various *Cyperus* species. The O-methylated flavone tricin is another widely distributed flavonoid compound reported in around 90 *Cyperus* species. The tetrahydroxy aurone 'aureusidin' is reported from around 60 *Cyperus* species. Apigenin, quercetin and kaempferol are other major flavonoids reported from Cyperaceae members (Gamal *et al.,* 2015).

**Stilbenes in Cyperaceae members:** Among the polyphenolic compounds, stilbene derivatives are important bioactive components reported in several Cyperaceae species (Gamal *et al.,* 2015; Giri *et al*., 2015; Dávid *et al.,* 2021). Stilbenes with 1,2 diphenylethylene nucleus is a class of plant phenolics that occur in a number of heterogeneous and phylogenetically unrelated plant families such as Cyperaceae, Dipterocarpaceae, Gnetaceae, Leguminosae, Polygonaceae and Vitaceae. Stilbenes, formed by the general phenylpropanoid pathway, are found as monomers, dimers and complex oligomers. Stilbenes are important from chemotaxonomic point of view, and they play a key role in plant defence mechanisms as well. The compounds are attributed with several pharmacological properties, and the monomeric stilbene trans-resveratrol is one of the most important bioactive phytochemicals with prominent role in the prevention and treatment of neurodegenerative diseases, diabetes and cancer. Resveratrol, the active molecule of red wine, is present in more than 70 plant species. Piceatannolis a monomeric stilbene, while scirpusins are dimerized stilbenes.

Stilbenes can be found in relatively high amounts in several Cyperaceae species, for instance the total content of stilbenes in the roots and rhizome of *Carex fedia* var. *miyabei* was estimated over 0.15% (w/w of fresh material), and in case of *Carex pumila*, the main constituent was miyabenol A present at 0.23% (w/w of dried material) in the plant. Dávid *et al.* (2021) has reviewed around 70 stilbenoids from 28 Cyperaceae members, of which around 18 were isolated from *Carex distachya*. Scirpusins A and B are abundant stilbene dimers in *Scirpus* and *Cyperus* species. *Cyperus longus, Cyperus capitatus, Cyperus conglomerates* and *Cyperus rotundus* are also reported to possess stilbenoids (Gamal *et al.,* 2015; Majeed *et al*., 2022).

The major stilbene derivatives reported from Cyperaceae plants are; hydroxy stilbenes (resveratrol, carexinols, scirpusins, 3,3',4,5'-tertrahydroxystilbene), prenylstilbenoids (carexanes), tetrastilbenes(cis-miyabenol A) and oligostilbenes (kobophenols, pallidolviniferins, smiglasids, virgatanol and piceatannol) (**Figure 2)** (Meng *et al*., 2001; Lee *et al*., 2013; Rajak and Ghosh, 2022). As Cyperaceae members are very good sources of a wide variety of stilbenes, and several of them occur in large quantity, they are worthy for further phytochemical and pharmacological investigations.



**Figure 2. A**- Hydroxy stilbene, resveratrol, **B**- Prenyl stilbene, carexane, and**C**-Tetrastilbene, cis-miyabenol A

**Discovery of novel prenylated cinnamates and stilbenes in** *Lepidosperma* **sp.** Propolis is the natural resinous mixture produced by honeybees from plants exudates, and is attributed with potential bioactivities, mainly due to the presence of characteristic polyphenols. The composition of propolis varies region wise, depending on the vegetation around. Propolis samples collected from the beehives of Kangaroo Island, Australia was found to have novel compounds belonging to prenylated cinnamate and stilbene classes (Abu-Mellal *et al.,* 2012). Ligurian honey bees, *Apis mellifera* sub sp. *ligustica* Spinola, were found to produce the propolis from the resin exuded by the Australian native sedge plant *Lepidosperma* sp. Montebello (Cyperaceae). There had been no previous reports of bees foraging for propolis on plants of the Cyperaceae family so these widespread plants had not been considered a likely source. Samples of plant exudates, resinous material carried on bee legs, and freshly deposited propolis in the hive were analysed by TLC and high field <sup>1</sup>H NMR spectroscopy, and found to be with similar chemical profile, with prenylated cinnamate and stilbene compounds (**Figure 3)** (Duke *et al.,* 2017).



**Figure 3.** Honey bee, propolis and stilbenes in *Lepidosperma* species

#### **Coumarins in Cyperaceae members**

Diversity of coumarin structures such as umbelliferone, xanthotoxol,  $7-(\gamma,\gamma)$ dimethylallyloxy)-8-methoxycoumarin, 7-methoxy-8- $(\gamma, \gamma$ -dimethylallyloxy) coumarin, 5,7dimethoxy-8- $(\gamma, \gamma$ -dimethylallyloxy) coumarin, prenyletin, leptodactylone, 5,7,8trimethoxycoumarin, 7,8-dimethoxycoumarin, 5,7-dimethoxycoumarin, scopoletin, and isoscopoletin have been reported from various *Cyperus* species such as *Cyperus alopecuroides, Cyperus incompletes* and *Cyperus papyrus* (**Figure 4)** (Mohamed *et al*., 2015)*.*



**Figure 4.** Coumarins reported from Cyperaceae members. **A-** Umbelliferone, **B-**Xanthotoxol, **C-** Prenyletin, **D-** Leptodactylone, and **E-** Scopoletin

**Quinones in Cyperaceae members:** Cyperaceae members have been shown to be prolific source of quinones with wide structural diversity such as difuran benzoquinones (Allan *et al.,* 1969; Allan *et al.,* 1978; Nassar *et al.,* 2002). Cyperaquinone, conicaquinone, scabiquinone, breviquinone, capiquinones and alopecuquinone are the major quinones reported from various Cyperaceae members (**Figure 5)** (Gamal *et al.,* 2015).



**Figure 5.** Major quinones reported from Cyperaceae members. **A-** Cyperaquinone, **B-**Scabiquinone, **C-** Capiquinone, and **D-** Alopecuquinone

*Cyperus capitatus* contains a homologous series of 11 6-alkyl-2-hydroxy-3-methyl-1,4 benzoquinones, with chain length C17 to C27 (Alves *et al.,* 1992).

# **Sesquiterpenoids in Cyperaceae members**

Sesquiterpenoids are abundant in the essential oils of various Cyperaceae members. *Cyperus articulates*, a common medicinal and aromatic species yielded several interesting sesquiterpenoids such as isopatchoul-4 (5) en-3-one, corymbolone,  $\alpha$ -corymbolol, mandassidione, isopatchoulenone and mustakone (Nyasse *et al.,* 1988). The systematic approach on the structure elucidation of complex sesquiterpenoids using conventional characterization techniques was revealed by the revision of the structure of the bicyclic ketone articulone isolated from *Cyperus articulates* to isopatchoul-4 (5) en-3-one. Couchman *et al*. (1964) proposed the structure as the bicyclic ketone articulone, which was further reinvestigated by Nigam (1965), Hikino *et al*. (1965), Nerali *et al*. (1965) and Neville *et al*. (1968) and confirmed the structure as isopatchoul-4 (5) en-3-one. *Scleria striatonux* rhizomes afforded novel bicyclic cyclofarnesyl endoperoxide class of sesquiterpenoids; okundoperoxide, sclerienone A-C (**Figure 6)** (Kennedy *et al.,* 2016).



**Figure 6.** Bicyclic cyclofarnesyl endoperoxide **A-**Okundoperoxide, **B-**Sclerienone A

#### **Diterpenoids inCyperaceae members**

Various Cyperaceae members have been reported as rich source of diterpenoids as well. The diterpenoids manoyloxide, 16-hydroxymanoyloxide, ll $\alpha$ -hydroxymanoyloxide, l $\beta$ - hydroxymanoyloxide, ambreinolide and norambreinolide were reported from *Kyllinga erecta* (**Figure 7)** (Dolmazon *et al*., 1995).



**Figure 7.** Major diterpenoids reported from *Kyllingaerecta*- **A-**Manoyloxide, **B**- 16- Hydroxymanoyloxide, C- llα-Hydroxymanoyloxide, D- lβ-Hydroxymanoyloxide, E-Ambreinolide and **F**- Norambreinolide

#### **Fatty acids in Cyperaceae members**

Fatty acids are extracted from the crude plant material by hexane solvent, and analysed by the GC-MS of volatilised Fatty Acid Methyl Esters (FAME). Generally, Cyperaceae members have the C18:3 fatty acid biosynthetic pathway as prominent. *Cyperus esculentus* is the major oil rich Cyperaceae member, and several reports are there on the oil composition of *Cyperus esculentus* (Lopéz-Cortés *et al.,* 2013). Ekeanyanwu and Ononogbu (2010) reported that the lipid found in *Cyperus esculentus* is non-drying and suitable for soap making. The fatty acid composition of *Cyperus esculentus* tuber oil (chufa oil) included oleic acid 689.2-732.9 g kg<sup>-1</sup>, palmitic acid 125.5-141.2 g kg<sup>-1</sup> and linoleic acid 99.6-154.6 g kg−1 , which is comparable with that of olive oil (**Figure 8)** (Coşkuner *et al.,* 2002).



**Figure 8.** The major fatty acids in *Cyperus esculentus,* oleic acid, palmitic acid and linoleic acid

The fatty acid profile of the leaves of *Cyperus laxus* showed palmitic acid, octadecanoic acid, oleic acid and eichosanoic acid. Casado *et al.,* (2015) showed that the weathered hydrocarbons drastically affect the lipidic composition of *Cyperus laxus* at the fatty acid level, suggesting that this species adjusts the lipid composition in its vegetative organs, mainly in roots, in response to the weathered hydrocarbon presence and uptake during the phytoremediation process. Bogucka-Kocka and Janyszek (2010) examined the fatty acid profiles of 13 *Carex* species and found linoleic acid, oleic acid, α-linolenic acid and palmitic acid as the major fatty acids.

For papyrus (*Cyperus papyrus*), the lipid content accounted for 4.1% in the rind and 4.9% in the pith, and several lipidic compounds such as hydrocarbons, fatty acids, 2 hydroxyfatty acids, fatty alcohols, phytol, phytol esters, alkylamides, glycerides, steroids, tocopherols and ferulates (Rosado *et al.,* 2022). n-Hexadecanoic acid, cis, cis-octadeca-9,12-dienoic acid, cis-octadec-9-enoic acid, n -octadecanoic acid, cis, cis-octadeca-9,12,15 trienoic acid were the major fatty acids in rind and pith of the plant.

# **Phytochemistry of** *Cyperus* **species other than** *Cyperus rotundus*

In addition to *Cyperus rotundus*, few other *Cyperus* species such as *Cyperus esculentus,Cyperus scariosus,Cyperus conglomeratus,Cyperus distans,Cyperus articulatus* and *Cyperus longus* have also been investigated in detail for the constituents. Gamal *et al.* (2015) and Taheri *et al.* (2021) have summarized the phytochemicals of different *Cyperus* species. Literature review revealed that 97*Cyperus* species have been investigated for their phytochemicals (**Table 1**). In addition to *C. rotundus, C. alopecuroides, C. alternifolius, C. articulates, C. conglomerates, C. difformis, C. dubius, C. esculentus, C. laevigatus, C. longus* and *C. scariosus* are the major species investigated for the phytochemicals.

*Cyperus esculentus***:** The plant, also known as tiger nut, earth almond or yellow nut sedge, has sweet tubers and reported to have health and nutritional benefits (Venkatachalam and Sathe, 2006; Zhang et al., 2022). The plant is also considered as the world's 16<sup>th</sup> worst weed (Holm *et al.,* 1977). The plant was cultivated in the Nile valley by ancient Egyptians, and was discovered in tombs in Egypt, and now the plant is being cultivated in several countries across the world, especially the Eastern Hemisphere, as animal feed, side dish for human consumption, and for preparing the beverage *Horchata*. The plantexists in three varieties; black, brown and yellow, amongst which the yellow one is the most solicited for human and animal consumption.

The plant has been reviewed intensively for its chemical constituents and potential biological activities (Zhang *et al.,* 2022). The findings of recent research showed high content of nutrients and bioactive phytochemicals such as alkaloids, glycosides, flavonoids, crude fibres, tannins, proteins, carbohydrates, oxalates, phytates and fats in tiger nut. The tuber is particularly rich in fixed oil, with high oleic acid content. The tuber of *Cyperus esculentus* is used as a snack and also for making a sweet and tasty beverage. *Horchata de chufa* is a traditional Spanish beverage produced from tiger nuts, and the drink is popular in Spain (Pascual *et al.,* 2000). In Cameroon, more than 17,000 tons tiger nuts are produced per year (Djomdi *et al.,* 2013). In Spain, around 8,360 tons of dried tiger nuts are produced annually, and the annual value of production in Spain has risen to 3.3 million Euros (Carlos *et al.,* 2022; Pelegrin *et al.,* 2022; *Zhang et al*., 2022).

The plant is a potential source of carbohydrates, fiber and polyphenols, and could be used as potential ingredients in the food industry (María del Carmen Razola-Díaz *et al.,* 2022). Tiger nuts are rich in carbohydrates (58.9%), lipids (24.5%), calcium (100.2 mg/100g), potassium (487.1 mg/100g), phosphorus (128.6 mg/100g), magnesium (94.8 mg/100g), but poor in proteins (8.1%) and zinc (4.0 mg/100g) (Okoye and Ene, 2018). Both the volatile and non-volatile phytochemicals were investigated in detail. The rhizome oils of two varieties (brown and black) of Nigerian *Cyperus esculentus* were found to be potential sources of  $\alpha$ -pinene (70.5-75.5%). In addition, different chemotypes have also been reported for these species (Kubmarawa *et al.,* 2005). Investigation of the ethanolic extracts identified more than 40 polyphenols with promising medicinal applications (Olukanni *et al.,* 2022; Pelegrin *et al.,* 2022; Diaz *et al.,* 2022).

*Cyperus scariosus*: Tubers of the plant is the source of cypriol oil, the essential oil with ambery, balsamic, spicy, warm and woody notes, which is widely applied in various perfumes and medicines and of high demand in perfume industry (Bhawna *et al.,* 2013; Kumar *et al.,* 2016). Kumar *et al.* (2016) analysed *Cyperus scariosus* oils from 13 locations in India and the oil yield varied from  $0.2$  to  $0.5$  %v/w. The major compounds were cyperene, longifolin, caryophyllene oxide and longiverbenone. Characteristic nitrogenous components such as epi-guaipyridine, guaia-9,11-dienpyridine and cananodine have been reported from *Cyperus scariosus* oil (**Figure 9)** (Clery *et al.,* 2016). Rotundone

was found as the volatile compound responsible for the woody amber odour of cypriol oil together with other ketones such as cyperen-8-one (Clery *et al.,* 2016).



**Figure 9.** Major nitrogenous components and odoriferous components identified in *Cyperus scariosus* essential oil. **A-** epi-Guaipyridine, **B**- Guaia-9,11-dienpyridine, **C**-Cananodine

*Cyperus articlulatus:* The tropical sedge *C. articlualtus* is widely used in traditional medicine, as well as in perfumery. Characteristic sesquiterpenoids such as isopatchoul-4 (5) en-3-one, corymbolone,  $\alpha$ -corymbolol and mandassidione were isolated from the rhizome essential oil (**Figure 10)** (Nyasse, 1988). The sesquiterpenoids cyperotundone, mustakone, 1,2-dehydro-α-cyperone and sesquichamaenol were identified as lead molecules in *Cyperus articulatus* with antiseizure activity (Brillatz *et al*., 2020).



**Figure 10.** Sesquiterpenoids reported from *Cyperus articulatus* with antiseizure activity. **A-** Cyperotundone, **B-** Mustakone, **C-** 1,2-Dehydro-α-cyperone, and **D-**Sesquichamaenol

*Cyperus conglomeratus*: The plant is another important *Cyperus* species with wide distribution, especially in the extreme dessert conditions, and has traditional medicinal uses such as analgesic, diuretic, stimulant, pectoral, emollient and anthelmintic and revealed pharmacological activities such as antimicrobial and anti-candidal properties. Cyperene was the major component of the rhizome essential oil of *Cyperus conglomeratus* collected from Iran (Feizbakhsh and Naeemy, 2011). In additional to essential oils, several metabolites such as flavonoids, triterpenoids, steroids and aromatic shikimates were isolated and characterized from the species (Abdel-Mogib *et al.,* 2000). Elshamy *et al.* (2020) reported 70 metabolites belonging to phenolic acids, organic acids, cinnamic acid derivatives, flavonoids, stilbenes, aurones, quinones, terpenes and steroids from *Cyperus conglomerates* through UPLC-qTOF-MS/MS analysis. The fatty acid profile of the tubers

comprised of mainly stearic acid, myristic acid, palmitolic acid and behenoic acid (Ghaferah *et al.,* 2018).

*Cyperus distans*: The plant, an annual herb, is native to tropical and subtropical wetlands. The phytochemical study of *Cyperus distans* revealed the presence of scabequinone with antifeeding effects (Morimoto *et al.,* 1999). Zierone has been identified as the major component of the rhizome essential oil (**Figure 11)** (Lawal and Oyedeji, 2009).



**Figure 11.** The quinone scabequinone and the sesquiterpenoid zierone reported from *Cyperus distans*

**Phytochemical studies on** *Carex* **species:** *Carex* L. with more than 2000 species is the largest genus of the family Cyperaceae, and also one of the largest vascular plant groups. They occur in very differentiated habitats, both in wet and moist localities and also in extremely dry habitats. The genus *Carex* has attracted the attention of phytochemists, especially due to the characteristic phenolic constituents. Literature review revealed that 53*Carex*species have been investigated for their phytochemicals (**Table 1**). Among various *Carex* species, the widely investigated species is *Carex distachya*.

Harborne (1971) had performed two-dimensional chromatographic investigation on the distribution of kaempferol, quercetin, glycoflavone, luteolin and tricin in leaf extracts of different *Carex* species. Bogucka-kocka *et al*. (2011) estimated the phenolic acids (caffeic, ferulic, p-coumaric, p-hydroxybenzoic, protocatechuic, sinapic, syringic and vanillic acid) in the aerial parts of 18 *Carex* species from Central Europe. Several new lignan glycosides and furofuran type lignan aglycones were reported from the polar extract of *Carex distachya* (Fiorentino *et al*., 2008). Ricci *et al*. (2008) investigated in detail the fragmentation pattern of the complex lignans by tandem mass spectrometry. Novel class of dibenzoxazepinones were also reported from the species (Fiorentino *et al*., 2007). Stilbenoid derivatives are another characteristic class of phenolics identified from several *Carex* species. Oligostilbenes formed by 2-4 monomers of resveratrol and tetracyclic

prenylated stilbenes are characteristic of the genus (D'Abrosca *et al*., 2005). The stilbenoidscaraxanes with unusual tetracyclic structure with a hydroxyl group at the C-3 carbon and a methoxyl group at the C-5 were reported from *Carex distachya* (**Figure 12)**.



**Figure 12.** Caraxanes A-C (1. Caraxane A, 2. Caraxane B and 3. Caraxane C)

**Phytochemical studies on** *Kyllinga* **species:** *Kyllinga,* frequently referred to as spike sedges, is another widely distributed genus in the Cyperaceae family. Alkaloids, coumarins, flavonoids, glycosides, lignins, phenols, steroids, tannins and terpenoids were reported from the genus (Verma *et al.,* 2017). The essential oil of fragrant kyllinga, *Kyllinga odorata* Vahl showed dihydrokaranone and aristolochene as the major compounds (Tucker *et al.,* 2006). Literature review revealed that 8 *Kyllinga* species have been investigated for their phytochemicals.

**Phytochemical studies on** *Rhynchospora* **species:** Though the genus *Rhynchospora* Vahl. is widely distributed globally, with about 270 species, it is least investigated for the phytochemicals, except for *Rhynchospora corymbosa* (Strong, 2006; Annie *et al*., 2016; Bezerra *et al*., 2019).

**Phytochemical studies on** *Scleria* **species:** The genus *Scleria*, commonly known as nutrush, consists of perennial herbs. *Scleria* has not attracted much attention from phytochemists, except for a few reports on essential oils. *Scleria striatonux* rhizome is used in some parts of Cameroon as a spice and possessed a very pronounced inhibitory activity. The rhizomes afforded novel bicyclic cyclofarnesyl endoperoxide class of sesquiterpenoids; okundoperoxide, sclerienone A-C (Kennedy *et al.,* 2016).

## **Phytoremediation potential of Cyperaceae species**

Hyperaccumulators can tolerate, take up and translocate high levels of certain metals that would be toxic to most organisms. Many of the Cyperaceae members have heavy metal phytoremediation potential from contaminated water sources and can be considered as hyperaccumulators. The sedge plant *Cyperus alopecuroides* was found as a powerful phytoremediator to remove heavy metals from contaminated water bodies. *Cyperus alopecuroides* roots accumulated concentrations of all measured heavy metals, except Ni, Cu, Zn, and Pb, more significant than the shoot. The bioconcentration factor was generally > 1, while the translocation factor of all elements, except Pb, was ˂ 1 (Galal *et al.,* 2021). It has been demonstrated that *Cyperus laxus* significantly reduces the hydrocarbon levels from soils containing up to 325,000 mg THC Kg-1 soil (Casado *et al.,* 2015). *Cyperus alternifolius* and *Cyperus dives* were found as effective phytostabilizers of Arsenic, Cadmium and Lead metals with greater than one biocentration factor values, while translocation factor values were less than one. *Cyperus alternifolius* also reduced significantly the total nitrogen content of the influent water in a vertical-flow constructed wetland model (Cui *et al.,* 2009). The plant was also efficient in removing phenolic compounds up to 98.8% from waste water. The plants accumulated trace elements, especially in the roots, with the order of Fe  $> Mn > Cu > Zn > B > Pb > Cr > Ni > Co > Cd$ (Goren *et al.,* 2021).*Cyperus rotundus* and *Cyperus alternifolius* were found to eliminate fluoride from water (Neetin Desai, 2020).

Evaluation of the phytoremediation potentiality of *Cyperus articulatus* revealed maximum accumulation for iron (105.5 and 900  $\mu$ g/g dry wt.) in wastewater, while minimum values were obtained for the accumulation of cadmium (0.9 to 1.95  $\mu$ g/g d.wt.), among the tested metals As, Cd, Cr, Cu, Fe, Hg, Mn, Ni and Pb (Farrag and Fawzy, 2012). *Cyperus articulatus* plants accumulated most of the heavy metals, except Pb, in their roots than in the shoots, and the bioaccumulation factor was  $> 1$ , and the translocation factor of most heavy metals, except Pb was <1 (Galal *et al.,* 2017).

# **Antifeedant, insecticidal and repellent phytochemicals in Cyperaceae species**

Cyperaceae are generally not affected by pests in upland and paddy fields, and are seldom damaged by phytophagous insects, because they contain insect antifeedants. Morimoto *et*  *al*., (1999) observed the insect repellent property of many of the *Cyperus* species and showed that the hexane extract of *C. amuricus, C. brevifolius, C. ceperinus, C. cyperoides, C. difformis, C. diffuse, C. distans, C. flavidus, C. haspan, C. iria, C. javanicus, C. microiria, C. monophyllus, C. nipponicus, C. nutans, C. odoratus, C. orthostachyus, C. pilosus, C. sanguinolentus, C. serotinus* and *C. stoloniferous* were strongly insect repellent. From the basal stem of *Cyperus nipponicus* and *Cyperus distans* the antifeedants remirol, cyperaquinone and scabequinone were identified (**Figure 13)** (Morimoto *et al*., 1999). Hexane extract of *Cyperus compresses* also possess strong insect repellent property (Al-Shamma *et al*., 1979). Hexane extract of *Cyperus rotundus* rhizomes was found to be effective against the mosquitos *Anopheles culicifacies, Anopheles stephensi* and *Culex quinquefasciatus*. *Cyperus rotundus* was found as more effective insecticidal than carbamate and has almost the same efficacy as that of organophosphate (Bañez and Castor, 2011). Essential oil of *Cyperus rotundus* rhizomes showed remarkable activities on eggs and instar larvae of *Aedes albopictus* (Imam and Chandra, 2014). The sesquiterpene ketone,  $\alpha$ -cyperone, a constituent of several Cyperaceae members showed significant insecticidal activity against diamond back moth (DBM) larvae (Dadang *et al.,*1996).



**Figure 13.** The antifeedants isolated from Cyperaceae plants. **A-** Remirol, **B-**Cyperaquinone and **C-** Scabequinone

# **Allelochemicals in Cyperaceae species**

Plants produce a wide variety of allelochemicals to protect themselves from pathogens, herbivores and from neighbouring plants. Allelochemicals are particularly significant in inhibiting the growth of neighbouring plants. The organic solvent extracts, essential oils and isolated compounds from various Cyperaceae members showed allelopathic properties, and several natural products, *viz*., coumarins, quinones and sesquiterpenes have been identified as potential allelochemicals (Dini *et al*., 1992; Dini *et al*., 1993). Morimoto and Komai (2005) reported that the sesquiterpenoids cyperotundone and α-cyperone produced in *Cyperus rotundus* can inhibit the growth of other plants nearby (**Figure 14)**. Stilbenoids

and flavonoids from *Carex distachya* have been shown to act as allelochemicals in the Mediterranean macchia vegetation (Fiorentino *et al*., 2008).



**Figure 14.** Allelochemicals in *Cyperus rotundus,* cyperotundone and α-cyperone

#### **Chemotaxonomic evaluation**

Plant chemosystematics is the application of chemical data to systematic problems, and explored for explaining relationships between plants and inferring phylogeny (Singh, 2016). Among secondary metabolites, flavonoids with wide structural features are more useful for studying relationships within the species and genus level (Harborne, 1994). Generally, the angiosperm flavonoid evolution involves a progressive reduction in the number of different flavonoid structural classes; the reduction of a flavonol-glycoflavone profile to glycoflavones alone is often used as an example.

Most of the systematic classifications of Cyperaceae are based on the classical taxonomic features, obtained as a result of morphological and anatomical analyses. However, the diversity of flavonoids, oligostilbenes, phenolic acids and fatty acids are described as useful chemotaxonomic markers for Cyperaceae. Flavonoids are common phytochemicals in Cyperaceae. Earlier studies on the flavonoid chemistry included generalized acidhydrolysis surveys of the Cyperaceae, that suggested possible putative relationships between the Cyperaceae, Gramineae and Juncaceae, but yielded little information below the generic level. Harborne *et al* have extensively studied the distribution pattern of flavonoids in around 100 Cyperaceae plants in Australia and arrived at significant correlations (Clifford and Harborne, 1969; Harborne, 1971; Harborne *et al.,* 1985).

Flavones, such as tricin and luteolin are very common in Cyperaceae species. Luteolin 5 methyl ether was found in several Cyperaceae genera, while luteolin 7-methyl ether, diosmetin and acacetin were limited in the Cyperaceae. Flavonols and their methyl ethers were detected in over one-third of the species, particularly in the leaves of the genera *Fuirena, Gahnia, Lepidosperma* and *Mesomelaena*. Myricetin was found only in

two *Baumea* species. The 3-desoxyanthocyanidin carexidin was found in the inflorescences of eight Cyperaceae species (Harborne *et al.,* 1985). The presence of the characteristic leaf flavonoids (glycoflavones, tricin) of the grasses showed that the Cyperaceae and the Gramineae are more closely linked chemically than a previous study of their inflorescence pigments suggested (Harborne, 1971). Aurone pigments, the most distinctive Cyperaceae family constituents, were found in the leaves of 25% of the species and in the inflorescences of 40% species. 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 (Allan *et al.,* 1978). The abundant aglycones of the inflorescence spike of Fraser's sedge (*Cymophyllus fraseri*) indicate a biochemical feature differentiating leaf and floral tissues. This is contrary to the general concept that high concentrations of water-soluble glycosides are expected in flower tissues (Robert and James, 1988). Among the five *Scirpus* species; *S. holoschenus, S. lacustris, S. littoralis, S. maritimus* and *S. multicaule* collected from Iran, all the taxa contain flavonoid sulphates, flavone C and C-/O-glycosides and aglycones, while *Scirpus maritimus* was distinct by the distribution of flavonoid aglycones (Noori *et al.,* 2012). Bogucka-Kocka *et al.* (2011) used phenolic acids from the aerial parts of *Carex* species as chemotaxonomic markers for delimitation of the species. However, several attempted tests of aggregative cluster analysis showed no similarity to the real taxonomical structure of the genus *Carex* with the phenolic acid distribution. There is scope for further investigation using modern analytical techniques such as LC-MS/MS, ambient analytical techniques and head space analytical techniques for the rapid comparison of various taxa among the Cyperaceae family.

## **Conclusions**

The Cyperaceae family is the  $10<sup>th</sup>$  largest flowering plant families and is ranked the third largest monocot family after Orchidaceae and Poaceae. Across the diverse traditional systems of medicine, plants coming under the Cyperaceae family are popularly employed as potent ethnomedicines owing to the plethora of pharmacological attributes and the presence of diverse phytochemicals. The highly potential trans-stilbene resveratrol and its derivatives are reported from several Cyperaceae members. However, though nearly 5,500 species are reported in the family, literature review revealed only 180 species have been

investigated phytochemically, and majority are studied for the volatile chemicals or distribution of flavonoids only. There is scope for detailed phytochemical studies involving solvent extraction, separation through various chromatographic techniques, and characterisation using different spectroscopic techniques, and also through modern hyphenated techniques such as LC-MS/MS and LC-NMR.

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