Phytochemistry, Vol. 24, No. 12, pp. 3077–3078, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00
Pergamon Press Ltd.

FLAVONOIDS OF *MAYACA FLUVIATILIS* (MAYACACEAE)*

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(*Received* 24 *April* 1985)

Key Word Index—*Mayaca fluviatilis*; Mayacaceae; bogmoss; flavonol glycosides; quercetin; kaempferol, flavone; luteolin 5-glucoside; chemosystematics.

Abstract—*Mayaca* is an aquatic monocot of the monogeneric family Mayacaceae. The flavonol glycosides quercetin 3-*O*-glucoside, quercetin 3-*O*-rutinoside, and kaempferol 3-*O*-glucoside, and the flavone luteolin 5-*O*-glucoside were found in methanolic leaf extracts. The presence of flavonol and flavone *O*-glycosides sets the Mayacaceae apart from the Commelinaceae, which accumulates predominantly flavone *C*-glycosides.

INTRODUCTION

Mayaca fluviatilis Aublet, bogmoss, is an aquatic vascular plant which grows either on mudflats or submersed in standing or flowing water. Most modern classifications place the Mayacaceae in the Commelinales with the Commelinaceae and a variable number of other families [1]. *Mayaca fluviatilis* is the most widespread species of the genus, ranging from the southeastern United States of America to Argentina. Several other species of the genus occur in Central and South America, with a single species endemic to southern Africa [2]. The only report of the flavonoid constituents of the genus is that of quercetin from *Mayaca sellowiana* Kunth in a survey by Bate-Smith [3].

RESULTS

Chromatographic separations of aqueous methanolic extracts of whole plants of *Mayaca fluviatilis* yielded four flavonoid compounds. Three were identified as flavonol 3-*O*-glycosides. They included kaempferol 3-glucoside, quercetin 3-glucoside, and quercetin 3-rhamnoglucoside (rutin). The fourth compound was a conspicuous fluorescent blue compound with the R_f values similar to luteolin. Spectral data, particularly the aluminium chloride and aluminium chloride–hydrochloric acid shifts, indicated that the compound was orthodihydroxylated and did not have a free 5-hydroxyl. Enzymatic and acid hydrolyses yielded luteolin as the aglycone, showing that the sugar was attached to the 5-hydroxyl of the A-ring. Acid hydrolysis of the glycoside yielded glucose, and β-glucosidase hydrolysed the glycoside. The blue compound is thus luteolin 5-glucoside. Other properties of the compound were in agreement with those reported by Glennie and Harborne [4]. Sulphated flavones, characteristic of many aquatic monocots, were not detected in *Mayaca*.

DISCUSSION

The taxonomic affinities of the Mayacaceae are somewhat uncertain [5], but modern classifications generally place the family with the Commelinaceae and a variable number of other families in the order Commelinales. Relationships have also been frequently suggested with the Xyridaceae and Eriocaulaceae. Although flavonoid data for only a small number of species of Commelinaceae [6], Xyridaceae, and Eriocaulaceae have been reported [7] flavonols are apparently rare and *C*-glycosylflavones common in all but the Eriocaulaceae. The occurrence of luteolin 5-glucoside is noteworthy because of the limited distribution of 5-*O*-substituents. Flavone 5-*O*-glycosides are known from a number of rather unrelated dicotyledonous families and from the monocotyledonous families Cyperaceae and Poaceae [4, 8]. The present limited chemical data indicate substantial dissimilarities between the flavonoids of the Mayacaceae and those reported from the Commelinaceae. However, luteolin 5-glucoside is likely to be much more frequent in the monocots than is presently known. It is very acid labile and many surveys of monocot groups have used hydrolytic methods. Given the rather unpredictable occurrence of 5-*O*-glycosides in the Dicotyledonae, it would be unwise to suggest a connection between the Mayacaceae and the Cyperaceae or Poaceae based on the occurrence of this compound.

EXPERIMENTAL

Plant material. Material was obtained from air-dried field collections. Florida: Santa Rosa Co., Branch of Big Juniper Creek, S 1/2 Sec 7 T5N, R21W. Growing in cold swift clear water 0.3–0.6 m deep. 19 Feb 1983. R. R. Haynes *8700*. Voucher specimens are at The University of Alabama Herbarium (UNA).

Isolation and identification. Soluble compounds were exhaustively extracted from 27 g of leaves and stems with 85% MeOH. Extracts were concd to water under vacuum, partitioned with $CHCl_3$, and repeatedly extracted with EtOAc, and each fraction checked by TLC on cellulose. EtOAc fractions were separated by 1D-PC and 2D-PC using TBA (*t*-BuOH–HOAc–H_2O, 3:1:1)

*Contribution number 84 from the Aquatic Biology Program, University of Alabama.

and 15% HOAc. Individual spots or complexes of compounds were eluted from sheets and further purified using cellulose and polyamide TLC and Sephadex LH-20 columns with standard solvent systems [9]. Compound identities were determined by standard techniques using R_f values, colour reactions, UV spectrophotometry with diagnostic reagents, and co-chromatography with known samples [9, 10]. Sugars of *O*-glycosides were identified by enzymatic hydrolysis with β-glucosidase and acid hydrolysis followed by circular co-chromatography with commercial standards [11].

Acknowledgements—NSF DEB 78-18402 and DEB 80-21387 to RRH.

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Phytochemistry, Vol. 24, No. 12, pp. 3078–3080, 1985.
Printed in Great Britain.

0031–9422/85 $3.00 + 0.00

QUERCETAGETIN 6,7,4′-TRIMETHYL ETHER AND 3-SULPHATE FROM *DECACHAETA HAENKEANA*

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(*Revised received* 26 *March* 1985)

Key Word Index—*Decachaeta haenkeana*; Compositae; Eupatorieae; 6-methoxyflavonols; flavonol sulphate.

Abstract—Four 6-methoxylated flavonols, including a new quercetagetin derivative and its 3-potassium sulphate salt, were isolated from the aerial parts of *Decachaeta haenkeana*.

INTRODUCTION

As part of our continuing chemotaxonomic study of the tribe Eupatorieae, we here report the isolation and characterization of four flavonols, including a new flavonol and its 3-*O*-sulphate, from the aerial parts of *Decachaeta haenkeana* DC., the type species of the genus. Although *Decachaeta* has been treated as monotypic by earlier authors [1], a revision by King and Robinson [2, 3] expanded the genus by including six additional species from *Ophryosporous* and *Eupatorium*. These authors maintain *D. haenkeana* in a separate subgenus (subgenus *Decachaeta*), while combining the six new species in a second subgenus, *Polydenia*. Preliminary chemical studies have lent some support to this distinction. The three species studies from subgenus *Polydenia*, *D. thieleana* [4, 5], *D. ovatifolia* [6] and *D. scabrella* [Miski *et al.*, unpublished], all contain sesquiterpene lactones mainly of the guaianolide type, although 7α-hydroxy lactones of several skeletal types are found in *D. ovatifolia* [6]. In contrast, we were unable to isolate any sesquiterpene lactones from *D. haenkeana*.

RESULTS AND DISCUSSION

The dichloromethane extract of *D. haenkeana* afforded one new as well as one known flavonol aglycone. The new flavonol aglycone was established as quercetagetin 6,3′,4′-trimethyl ether (**1**) by the following spectral data. When the compound was viewed on paper under UV light it exhibited a faint yellow colour with and without ammonia which did not change when sprayed with NA reagent.