Pergamon

0031-9422(95)00527-7

Phytochemistry, Vol. 40, No. 5, pp. 1579-1580, 1995

6,3′,4′-TRIHYDROXY-4-METHOXY-5-METHYLAURONE FROM *CYPERUS CAPITATUS*

Rosa M. Seabra, M. Manuela Moreira, M. A. Cruz Costa and M. Isabel Paúl

CEQUP/Faculdade de Farmácia do Porto, Laboratório de Farmacognosia, Rua Anibal Cunha, 4050 Porto, Portugal

(*Received in revised form 5 June 1995*)

Key Word Index—*Cyperus capitatus*; Cyperaceae; flavonoids; aurones; 6,3′,4′-trihydroxy-4-methoxy-5-methylaurone.

Abstract—An aurone has been isolated from *Cyperus capitatus* which was identified by spectral means as 6,3′,4′-trihydroxy-4-methoxy-5-methylaurone.

INTRODUCTION

The presence of quinones in the underground organs of several taxa of Cyperaceae has been reported [1]. In *Cyperus capitatus* Vandelli, dialkyl-hydroxy-*p*-benzoquinones have already been isolated by us [2]. With the exception of rhamnetin 3-rhamnosyl(1–4)rhamnoside which was isolated from tubers of *C. rotundus* [3], the flavonoids so far reported in this family were located in the aerial organs [4, 5]. In this study we report the isolation and identification of 6,3′,4′-trihydroxy-4-methoxy-5-methylaurone from *C. capitatus*, the first aurone isolated from underground organs of *Cyperus* spp.

RESULTS AND DISCUSSION

The reported compound was isolated from a methanolic extract of dried underground organs of *C. capitatus*, although it was also detected on TLC of the chloroform extract of the sample analysed. It showed a yellow colour in visible and UV light (366 nm) and turned orange on exposure to ammonia vapour or when sprayed with NA (Naturstoffreagenz A) on TLC cellulose plates. The R_f values on TLC (cellulose) were as follows: BAW: (0.64), 60% acetic acid (0.40); these values remained unchanged after heating with HCl.

Its UV–VIS spectrum showed: UV λ methanol nm: 270, 398; + sodium methoxide: 272, 446 (increased intensity stable for 5 min); $AlCl_3$: 263, 279, 432; + $AlCl_3$ + HCl: superimposable to that obtained with methanol; + sodium acetate: 279, 328sh, 420; + sodium acetate + H_3BO_3: superimposable to that obtained with sodium acetate. Both the colours obtained on chromatography and the spectrophotometric behaviour suggested an aurone with *o*-hydroxyls on the B ring and the absence of a hydroxyl group at C-4 [6]. These suggestions were supported by ^1H and ^{13}C NMR, which permitted the determination of the whole structure.

The ^1H NMR spectrum exhibited the pattern of a B ring of the catechol type with δ7.42 (1H, *d*, $J = 2$ Hz, C-2′), 7.19 (1H, *dd*, $J = 6.9$ Hz and 2Hz, C-6′), 6.82 (1H, *d*, $J = 6.9$ Hz, C-5′), and also signals at δ4.03 (*s*, 3H, Ar-OCH_3), δ1.9 (*s*, 3H, Ar-CH_3) and δ6.54 (*s*, 2H), which can be explained by the benzylic proton superimposed to an Ar-H from ring A. Values from ^{13}C NMR (Experimental) confirmed all data presented so far; moreover, observed shifts showed the most common 4,6 oxygenated pattern on ring A. Assuming the UV spectrum from $AlCl_3$ + HCl, we can suggest that the compound has an 4-OCH_3 and a 6-OH. We located the methyl group on C-5 after the following observations: (i) assuming the values from sulfuretin [7] and the shifts caused by the addition of radicals [8], we can suggest that the values obtained from ring A are in agreement with the theoretical 4-OMe-5-Me-sulfuretin rather than with a 4-OMe-7-Me-sulfuretin; (ii) in accordance with Markham *et al.* [9] the registered value of δ61.43 for $O\underline{C}H_3$ is due to a 'sterically crowded methoxyl' near a methyl group (if there was a -H at C-5 value for $O\underline{C}H_3$ there would be 5 ppm upfield). Data from mass spectrometry was consistent with the fragmentation pattern of a flavonoid [10]. These observations suggest that the product is 6,3′,4′-trihydroxy-4-methoxy-5-methylaurone, and, as far as we know this is the first time this compound has been isolated.

EXPERIMENTAL

Plant material. *C. capitatus* was collected from sandy soils on the seaside near Aveiro, in 1990, and it was classified at the Botanic Institute of Oporto University by Prof. Barreto Caldas.

Extraction and purification. Ground rhizomes and roots were repeatedly macerated with $CHCl_3$ followed by maceration with MeOH. The brown methanolic extract was submitted to prep. TLC (cellulose, 0.30 mm) using BAW and 60% HOAc until the compound was pure. Elution from cellulose was carried out with MeOH.

General methods. TLC spray reagents and UV analysis were used as reported elsewhere [6]. NMR spectra were recorded at 300 MHz (^{1}H) and 75.47 (^{13}C) in DMSO-d_6 (δ ppm, TMS as int. standard).

^{13}C NMR data. δ145.52* (C-2), 178.76 (C-3), 156.86 (C-4), 116.05 (C-5), 165.12† (C-6), 93.26 (C-7), 165.63† (C-8), 105.50 (C-9), 110.94 (C-10), 123.59 (C-1′), 111.40 (C-2′), 145.55* (C-3′), 147.80 (C-4′), 117.66 (C-5′), 124.3 (C-6′) (*†assignments may be reversed). EIMS *m/z* (rel. int.): $C_{17}H_{14}O_6$, (found: 314.0763; calc.: 314.0790) $[M]^+$ (90), 313 $[M-1]^+$ (43), 285 $[M-HCO]^+$ (12), 180 $[A_1]^+$ (34), 181 $[A_1+H]^+$ (100), 134 $[B_1]^+$ (40), notations according to ref. [10].

Acknowledgements—We thank Prof. Barreto Caldas, from the Botanic Institute 'Dr Gonçalo sampaio', for plant classification and Department of Chemistry, UA, for MS.

REFERENCES

1. Allan, R. D., Wells, R. J., Correll, R. L. and MacLeod, J. K. (1978) *Phytochemistry* **17**, 263.
2. Alves, A. C., Moreira, M. M., Paúl, M. I. and Costa, M. A. C. (1992) *Phytochemistry* **31**, 2825.
3. (1987) *Chem. Abstr.* **106**, 15750.
4. Harborne, J. B. (1971) *Phytochemistry* **10**, 1569.
5. Harborne, J. B., Williams, C. A. and Wilson, K. L. (1985) *Phytochemistry* **24**, 751.
6. Markham, K. R. (1982) *Techniques of Flavonoid Identification.* Academic Press, London.
7. Markham, K. R. and Chari, V. M. (1982) in *The Flavonoids—Advances in Research* (Harborne, J. B. and Mabry, T. J., eds), Chapman and Hall, London (spectrum n° 97).
8. Markham, K. R. and Chari, V. M. (1982) in *The Flavonoids—Advances in Research* (Harborne, J. B. and Mabry, T. J., eds), p. 23. Chapman and Hall, London.
9. Markham, K. R. *et al.* (1987) *J. Plant Physiol.* **131**, 45.
10. Mabry, T. J. and Markham, K. R. (1975) in *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds). Chapman and Hall, London.