

Stilbenes and a New Acetophenone Derivative from *Scirpus holoschoenus*

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Abstract: Separation of the extract of the tubers of *Scirpus holoschoenus* L. (family Cyperaceae), a species easily confused with *Juncus* plants, afforded 2-prenyl-3,5,4'-trimethoxystilbene, 2-prenyl-3-hydroxy-5,4'-dimethoxystilbene, 2-prenyl-3,4'-dihydroxy-5-methoxy-stilbene and 3,5,4'-trimethoxystilbene, in addition to a new acetophenone derivative. The isolated compounds were identified on the basis of spectral measurements.

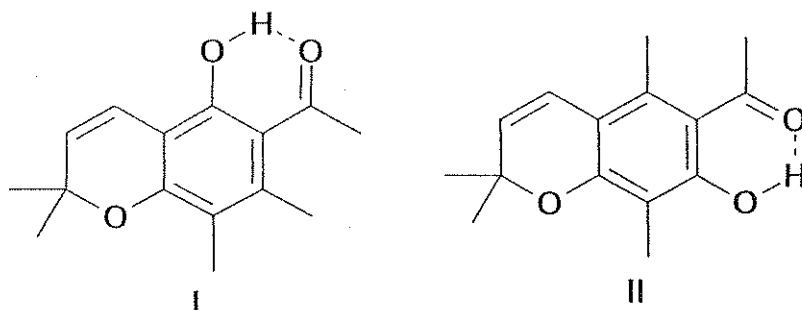
Keywords: *Scirpus holoschoenus*, Cyperaceae, stilbene, prenylstilbenes, acetophenone derivative.

Introduction

Scirpus holoschoenus L. (family Cyperaceae) is a rare, salty-marsh, perennial, ca. 1 meter high grass-like herb. Morphologically, it could be easily confused with *Juncus* (rush; family Juncaceae) because it is devoid of the characteristic solid three-angled stem of *Scirpus* [1], having instead a hollow cylindrical stem.

From the phytochemical point of view, *S. holoschoenus* had not been previously investigated. Moreover, only a few species of the genus *Scirpus* have been investigated for their chemical constituents. Derivatives of benzaldehyde, hydroxybenzoic acid and cinnamic acid were isolated from the rhizomes of *S. lacustris* [2]. Caffeic and coumaric acids were identified from *S. wichurai* [3]. Two stilbene dimers, scirpusin A and B, together with resveratrol, 3,3',4,5'-tetrahydroxystilbene and

(pair of doublets) at δ 5.51 and δ 6.68 ppm, with *cis* coupling of 10 Hz, in agreement with a *cis* 1,2-disubstituted ethylene moiety. There was also a singlet far downfield at δ 13.59 ppm, which was assigned to a hydroxyl group *ortho* to the methyl ketone. Thus, among the possible partial structures, I and II, benzopyrans additionally substituted with a methyl group and a methoxyl group, were more likely.



The NOESY spectrum of 5 revealed the presence of a NOE effect between the methoxyl group and both the methyl and the methyl ketone. This indicated that the methoxyl group was flanked by the methyl ketone from one side and the methyl from the other side. Thus 5 was assigned as 2,2-dimethyl-5-hydroxy-6-acetyl-7-methoxy-8-methyl-2-H-benzo[b]pyran. Other NOE effects were found between H-10 and the gem-dimethyl group (H-12, H-13), between H-9 and the methyl ketone (H-8) as well as between H-9 and H-10.

Table 1: ^1H -, ^{13}C -NMR data of compound 1

Atom No.	δ -value of ^1H -, multiplicity (J Hz)	δ -value of ^{13}C -, multiplicity*
1	—	124.30 [§] s
2	—	161.15 s
3	—	123.67 [§] s
4	—	158.56 s
5	—	122.08 s
6	—	158.75 s
7	—	203.49 s
8	2.67, s	31.30 q
9	6.68 d (10)	116.16 d
10	1.57, d (10)	126.62 d
11	—	73.72 s
12	1.45, s	28.44 q
13	1.45, s	28.44 q
14	2.05, s	8.37 q
OCH ₃	3.73 s	61.49 q
OH	13.61 s	—

* multiplicity was concluded from DEPT 90 and DEPT 135 experiments.

[§]exchangeable pair.

The proposed structure of 5 was also supported by the MS spectrum, that gave a molecular ion peak M^+ at m/z 262, in agreement with $C_{15}H_{18}O_4$, in addition to a base peak at m/z 247, due to the loss of a methyl group, and ion peaks at m/z values 229, 217 due to loss of H_2O and CH_2O from the ion 247, respectively.

Conclusions

The findings in this work indicate that the chemistry of *S. holoschoenus* is homogeneous with that of Cyperaceae [12] and different from that of Juncaceae [13,14].

Experimental

General

GC/MS spectra were taken on a QP-7000 Shimadzu instrument equipped with a fused silica capillary column (30 m x 0.25 mm ID), film (5% phenyl, 95% methylsilicon) thickness 0.25 μ , and processed using an IBM computer with software Class 500 and NIST library for comparison; NMR spectra were recorded on a Bruker FT-400 MHz (400 MHz for 1H - and 100 MHz for ^{13}C -, $CDCl_3$ solutions); IR spectra were taken on a Nicolet Magenta 550 FT IR spectrometer.

Plant material and processing

Scirpus holoschoenus L. was collected from Wadi Hetan, AlTaief-AlShafa road, Saudi Arabia, in November 1999 and identified by Prof. Dr. A. Faied, Botany Department, Faculty of Science, King Abdulaziz University. A voucher specimen was deposited at the Herbarium of King Abdulaziz University. Air-dried rhizomes (282 g) were extracted by soaking at room temp. in 1:1:1 MeOH/ether/petroleum ether for 24 hrs. The crude extract, obtained by evaporation, was defatted by dissolving in MeOH and leaving in the fridge-freezer for 24 hrs., then quick filtration and evaporation gave the final defatted extract (27.2 g, 9.6%).

Separation of compounds

The defatted extract was fractionated by silica gel column chromatography (CC) into five fractions (Sh1-Sh5), eluted by 9:1 petroleum ether/ether, 3:1 petroleum ether/ether, 1:1 petroleum ether/ether, ether and 9:1 ether/MeOH, respectively. Fraction Sh1 was obtained from the CC as two successive subfractions, Sh1a and Sh1b. Subfraction Sh1a (60 mg) contained fats. Subfraction Sh1b (72 mg) was further separated by TLC (silica gel, 9:1 petroleum ether/ether) into fat (35 mg, R_f 0.59), 5 (12 mg, R_f 0.54) and 2 (14 mg, R_f 0.51). Fractions Sh2 (170 mg) and Sh3 (100 mg) contained mainly compound 1. Fraction Sh4 was obtained from the CC as three successive subfractions Sh4a (1.5 g), Sh4b (5.1 g) and Sh4c (2.5 g). Subfraction Sh4a was purified by TLC (silica gel, 1:9 petroleum ether/ether) to give 3 at R_f 0.75. A 40 mg sample of subfraction Sh4b was separated by TLC (silica gel, petroleum ether/ether 1:4) into 2 (19 mg, R_f 0.96), 3 (8 mg, R_f 0.93) and 4a (7 mg, R_f 0.72). Subfraction Sh4c

contained mainly 4a. Compound 4a was refluxed with acetic anhydride for 1 hr. Evaporation to dryness afforded 4b. Fraction Sh5 (8.6 g) contained an unresolved complex mixture of pigments.

2,2-Dimethyl-5-hydroxy-6-acetyl-7-methoxy-8-methyl-2-H-benzo[b]pyran (5).

Yellow viscous oil; IR, $\nu_{\max}^{\text{CHCl}_3}$, cm^{-1} : 3553.3 (OH), 2928.3, 2856.2 (str. CH, CH₃), 1731.9 (C=O), 1613.3 (C=C), 1455.0, 1400.1, 1277.3, 1194.3, 1166.7, 1120.5, 1039.8, 1000.7, 892.6, 748.7, 697.3, 632.8; ¹H NMR: (Table 1); ¹³C NMR: (Table 1); MS, m/z (rel. int.): 262 [M]⁺ (19.1) (corresponding to C₁₅H₁₈O₄), 247 [M-Me]⁺ (100), 229 [247-H₂O]⁺ (17.5), 217 [247-CH₂O]⁺ (8.7), 115 (11.1), 91 (13.3), 77 (9.5), 43 (74.6).

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Sample availability: Samples of the isolated compounds are available from the authors.