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PHENYLPHENALENONES FROM *ENSETE VENTRICOSUM*

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Key Word Index—*Ensete ventricosum*; Musaceae; phenylphenalenones.

Abstract—The occurrence of compounds of the phenylphenalenone type in *Ensete ventricosum* (Musaceae) has been detected for the first time. One novel phenylphenalenone and two compounds already known from the Haemodoraceae and other species of the Musaceae were isolated. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

Ensete ventricosum (Welw.) is a member of the Musaceae family. It is cultivated in the south-western area of Ethiopia. The Gurage and related Ethiopian tribes use these plants as a main source for the production of starchy foods and beer. This plant species plays an important role in the daily life of the *Ensete* cultivating Ethiopians also with respect to the religious traditions and social organization. In traditional medicine of the Gurage the roots of *Ensete* are used to cure all forms of diseases [1, 2]. Phenylphenalenones are described to possess antitumor and antibacterial [3], nematicidic [4], antifungal [5] and photodynamic [6] activities. Although phenylphenalenones have been detected in the related genus *Musa* [7, 8], their occurrence in *Ensete* species hitherto has not been described.

RESULTS AND DISCUSSION

The roots and the rhizomes of plants of *Ensete ventricosum* were extracted with ethanol and the combined extract was partitioned between *n*-hexane–H_2O and $CHCl_3$–H_2O. The organic extracts were further separated by medium pressure liquid chromatography (MPLC) on a reversed phase column followed by preparative TLC on silica gel and finally purified by reversed phase HPLC.

2-Hydroxy-9-phenylphenalenone (anigorufone, **1**), which is a known compound of *Anigozanthos rufus* [9], *Musa acuminata* [8] and *Anigozanthos preissii* [10], was identified as a constituent of the *n*-hexane fraction. Compound **1** has recently been shown to possess nematicidic activity [4]. The chloroform extract contained 2-hydroxy-9-(4-hydroxyphenyl)-phenalen-1-one (hydroxyanigorufone, **2**) as the major compound. This phenylphenalenone was first isolated from *A. rufus* [9] and also has been detected in *Conostylis setosa* [3], *Musa acuminata* [11] and *A. preissii* [10]. The isolation of 8-hydroxy-7-methoxy-6-phenylphenalen-1-one (**3**) is described here for the first time. This minor compound was also found in the chloroform extract. A similar phenylphenalenone also bearing the phenyl group at C-6 was recently found in root cultures of *A. preissii* [10].

The structure of compound **3** was established by means of 1D and 2D NMR spectra and EI-MS (m/z 302, [M^+]). The signal of the carbonyl atom (C-1, δ 183.6) showed ^1H–^{13}C three-bond long range correlations (HMBC) with a doublet due to H-3 (δ 7.96) and a singlet due to H-9 (δ 8.19). The signal of H-2 (δ 6.64) was assigned on the basis of the chemical environment, ^1H–^1H COSY correlation with H-3 and HMBC cross signals with C-3a (δ 126.7) and C-9a (δ 125.4). The *peri* position of H-3 with H-4 (δ 7.84) was confirmed by mutual HMBC cross signals. The hydrogen atoms H-3, H-4 and H-9 showed HMBC connectivities with a common carbon atom (δ 123.0) which was therefore assigned to the central carbon C-9b. Furthermore, HMBC cross signals of the doublet of H-5 (δ 7.35) with C-1′ (δ 143.2), C-6a (δ 125.6) and C-3a were also in agreement with the suggested structure. The multiplet centered at δ 7.40 and integrating for five hydrogen atoms was readily assigned to the phenyl

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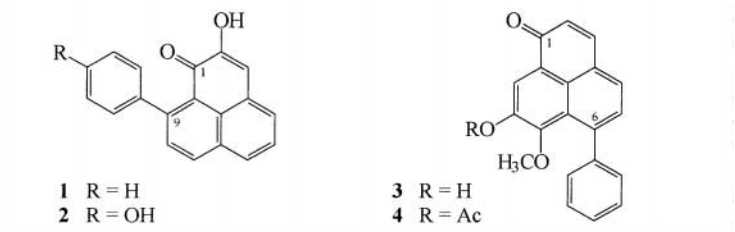

ring. The HMBC spectrum provided evidence for the position of the phenyl ring at C-6 (δ 142.1) by correlation of H-4 and hydrogen atoms of the phenyl ring (H-2′/6′) with C-6. HMQC correlations completed the assignments of the protonated carbon atoms. The chemical shift of the singlet at δ 3.23 integrating for three hydrogen atoms is typical for methoxyl groups in *peri* position relative to a phenyl ring [12], indicating that this methoxyl must be attached to C-7. Three-bond HMBC correlations of the methoxyl signal (δ 3.23) and of H-9 with the carbon signal at δ 149.1 designated this carbon atom as C-7. Acetylation of compound **3** indicated a hydroxyl group which finally had to be assigned to the remaining carbon atom C-8. The chemical shift of the methoxyl signal of the acetyl derivative **4** appeared at δ 3.34 again confirming the *peri* position of the methoxyl to the phenyl ring.

Despite the ethnobotanical importance of *Ensete ventricosum* in Ethiopia, the occurrence of phenylphenalenones in that species hitherto was not known and, moreover, has been reported here for the first time for the genus *Ensete*.

EXPERIMENTAL

Plant material

The seeds of *Ensete ventricosum* (Welw.) were obtained from H. Benary, Hannoversch Münden (Germany). After 14 d soaking in water the germinating seeds were planted into soil and grown under greenhouse conditions at a minimum temperature of 15°C. In summertime plants were cultivated outdoors. The voucher specimen has been deposited at the Institute of Plant Biochemistry Halle, Germany.

Isolation and purification

Rhizomes and roots of two years old plants (6 kg fr. wt) were chopped and exhaustively extracted with EtOH at room temp. The EtOH extract was evapd (< 40°C) and partitioned between *n*-hexane–H_2O and $CHCl_3$–H_2O. MPLC: RP-18; initial eluent EtOH–H_2O (1:1), stepwise increase of the EtOH–H_2O ratio to 1:0. TLC: silica gel 60 F_{254}; toluene–Me_2CO (4:1) and (2:1), respectively. Prep. HPLC: Nucleosil 7 C 18 (250 × 20 mm); MeCN–H_2O (17:3); UV 284 nm. The amounts of isolated compounds were as follows: **1**: 1.8 mg, **2**: 1.6 mg, **3**: 0.8 mg. Analyt. HPLC: LiChrospher 100 RP-18 (250 × 4 mm), 5 μm; gradient MeCN–H_2O (0.1% TFA) from 1:1 to 4:1 in 20 min and 9:1 in 25 min; UV 284 nm; 0.8 ml min^{-1}; compound **1**: R_t 20.6 min, **2**: 10.8 min, **3**: 13.5 min.

NMR spectrometry

NMR (Bruker DRX 500): 500.13 MHz (^{1}H), 125.75 MHz (^{13}C), TMS as int. standard. ^{1}H-NMR, ^{1}H–^{1}H COSY, HMBC and HMQC experiments were recorded in a 2.5 mm inverse detection microprobe head; broadband decoupled ^{13}C spectra were run using a 2.5 mm broadband microprobe head.

Compounds **1** *and* **2**

Analytical data of compounds **1** and **2** exactly matched those of the reference compounds previously isolated from *A. preissii* [10].

8-*Hydroxy*-7-*methoxy*-6-*phenylphenalen*-1-*one* (**3**)

Yellow needles, m.p. 259–261°C (CH_2Cl_2). EIMS (70 eV): *m/z* (rel int.) 303 (27) [(M + 1)$^+$], 302 (100) [M$^+$], 287 (87), 271 (7), 259 (16), 242 (7), 213 (10), 202 (14); UV λ_{max}^{MeOH} nm (ε): 215 (2.9), 267 (3.6), 428 (2.4); IR ν_{max}^{KBr} cm^{-1}: 2925, 1632, 1560, 1384, 1295, 1219, 854, 761; ^{1}H-NMR (DMSO-d_6): H-2 (δ 6.64, *d*, *J* = 9.7 Hz), H-3 (δ 7.96, *d*, *J* = 9.7 Hz), H-4 (δ 7.84, *d*, *J* = 7.3 Hz), H-5 (δ 7.35, *d*, *J* = 7.3 Hz), H-9 (δ 8.19, *s*), phenyl-H$_5$ (δ 7.40), MeO (δ 3.23); ^{13}C-NMR (DMSO-d_6): C-1 (δ 183.6), C-2 (δ 127.8), C-3 (δ 142.2), C-3a (δ 126.7), C-4 (δ 129.6), C-5 (δ 130.1), C-6 (δ 142.1), C-6a (δ 125.6), C-7 (δ 149.1), C-8 (n.d. because of poor signal to noise ratio and/or overlapping with C-7), C-9 (δ 121.6), C-9a (δ 125.4), C-9b (δ 123.0), C-1′ (δ 143.2), C-2′/6′ (δ 128.4), C-3′/5′ (δ 127.1), C-4′ (δ 126.6), MeO (δ 59.9).

Compound **4**

Compound **4** was prepared by acetylation of **3** with Ac_2O–pyridine (1:1) for 2 h at room temperature; EI-MS (70 eV): *m/z* (rel. int.) 344 (26) [M$^+$], 302 (100) [M$^+$-acetyl]; ^{1}H NMR (Me_2CO-d_6): H-2 (δ 6.66, *d*, *J* = 9.6 Hz), H-3 (δ 7.98, *d*, *J* = 9.6 Hz), H-4 (δ 7.97, *d*, *J* = 7.3 Hz), H-5 (δ 7.47, *d*, *J* = 7.3 Hz), H-9 (δ 8.34, *s*), Phenyl-H$_5$ (δ 7.43), MeO (δ 3.34), acetyl protons (δ 2.39).

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