

Chemistry Department, Faculty of Science, King Abdulaziz University, Jeddah, Saudi Arabia

## Two new naphthalene and anthraquinone derivatives from *Asphodelus tenuifolius*

M. ABDEL-MOGIB and S. A. BASAIF

Chromatographic separation of an ethanolic extract of rhizomes of *Asphodelus tenuifolius* Cav. (Asphodelaceae) yielded in addition to  $\beta$ -sitosterol, stigmasterol and two anthraquinone derivatives, 1,8-dimethoxynaphthalene as well as two new naphthalene derivatives. The new compounds were identified as 2-acetyl-8-methoxy-3-methyl-1-naphthol and 2-acetyl-1,8-dimethoxy-3-methylnaphthalene. The separated compounds were identified on the basis of IR, MS,  $^1\text{H}$  and  $^{13}\text{C}$  NMR data.

### 1. Introduction

The genus *Asphodelus* was considered as belonging to the family Liliaceae, but very recently, it has been separated as a distinct family, Asphodelaceae [1].

Some *Asphodelus* species have been reported to contain anthraquinone [2–10] as well as bianthrone [6, 11] derivatives. Essential oil from the aerial parts of *A. microcarpus* has been found to be antimicrobial [8], while the extract of the flowering aerial parts of *A. fistulosus* has been reported to be antifungal [7]. The flowery apexes of *A. albus* showed great anti-inflammatory activity [12]. The plant under investigation, *A. tenuifolius* has been investigated only in respect of lipids from its seeds [13].

In this paper, we present the isolation and identification of some anthraquinones and naphthalene derivatives.

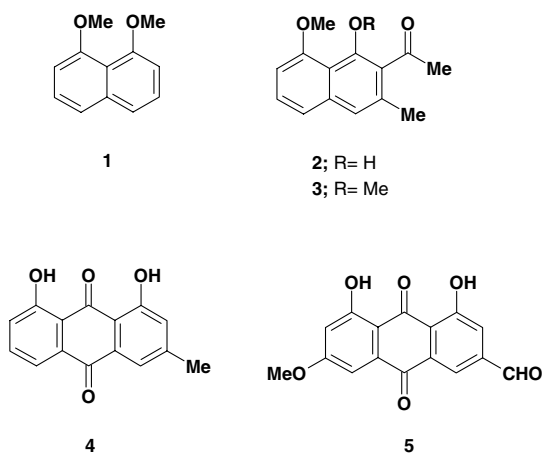
### 2. Investigations, results and discussion

Chromatographic separation of an ethanolic extract of rhizomes of *A. tenuifolius* yielded 1,8-dimethoxynaphthalene (**1**) [14], previously isolated from *Daldinia concentrica* [15], chrysophanol (**4**), previously isolated from *A. microcarpus* [2], fallacinal (**5**), previously isolated from the lichen *Cetraria cucullata* [16],  $\beta$ -sitosterol and stigmasterol [17], in addition to two new naphthalene derivatives **2** and **3**.

The  $^1\text{H}$  NMR spectrum of **2** (Table) showed signals of an aromatic methyl group ( $\delta$  2.37, s, 3H), an acetyl group ( $\delta$  2.63, s, 3H), a methoxyl group ( $\delta$  4.07, s, 3H), four aromatic protons (from  $\delta$  6.5 to  $\delta$  7.5) and an aldehydic or hydroxyl group as a singlet at  $\delta$  9.74 ppm. The presence of an IR absorption band at  $3362.8\text{ cm}^{-1}$  and the disappearance of the proton singlet at  $\delta$  9.74 in  $\text{D}_2\text{O}$  confirm the existence of a hydroxyl group. Thus an acetyl-, hydroxy-, methoxy-, methylnaphthalene derivative is most

**Table:**  $^1\text{H}$  NMR data of compounds **2** and **3** ( $\delta$ -value, multiplicity (J Hz), 400 MHz,  $\text{CDCl}_3$ )

H-atom	2	3
H-4	7.10 brs	7.39 brs
H-5	7.30 d (7.70)	7.33 d (7.70)
H-6	7.33 t (7.7)	7.38 t (7.7)
H-7	6.76 d (7.7)	6.84 d (7.7)
OCH <sub>3</sub>	4.07 s	4.02 s
	—	3.82 s
OH	9.74 s	—
CH <sub>3</sub>	2.37 s	2.35 s
COCH <sub>3</sub>	2.63 s	2.61 s



probable. The MS gave the expected molecular ion peak,  $\text{M}^+$  at  $m/z$  230 and a base peak (100%) at  $m/z$  215 due to  $\text{M}-\text{CH}_3$ . Comparing the results with literature data, the compound was assigned as the 8-methyl ether of the known naphthalene derivative musizin, previously isolated from *Rhamnus procumbens* [18].

The  $^1\text{H}$  NMR spectrum of **3** (Table) was similar to that of **2**, with the hydroxyl group singlet at  $\delta$  9.74 no longer present and a further methoxyl group singlet at  $\delta$  3.82. Thus, a dimethyl ether of musizin [18] is proposed. No hydroxyl group absorptions were seen in the IR spectrum. The MS confirmed the proposed structure. The molecular ion, at  $m/z$  244 due to  $\text{C}_{15}\text{H}_{16}\text{O}_3$ , gave a base peak (100%) at  $m/z$  229 by loss of a methyl group. The  $^{13}\text{C}$  NMR chemical shifts (Experimental) were in agreement with the proposed structure.

Some naphthalene derivatives have been isolated from *Daldinia* [15], *Rhamnus* [18] and *Diospyros* [19] species. This is the first report of naphthalene derivatives from the genus *Asphodelus*.

### 3. Experimental

#### 3.1. General

GC/MS spectra were recorded on a QP-7000 Shimadzu, with a fused silica capillary column (30 m  $\times$  0.25 mm ID), film thickness 0.25  $\mu\text{m}$  (5% phenyl, 95% methylsilicon), and evaluation on an IBM computer with Class 500 software and a NIST library for comparison; NMR spectra were recorded on a Bruker FT-400 MHz; IR spectra were taken on a Perkin Elmer Spectrum RX FT IR spectrometer.

#### 3.2. Plant material

*Asphodelus tenuifolius* Cav. (Asphodelaceae) was collected in April 2000 from Al-Shaffa top, the ring road, K.S.A., and identified by Prof. Dr. Ab-

delaziz Faied, Botany Department, Faculty of Science, King Abdulaziz University. A voucher specimen was deposited at the Herbarium of King Abdulaziz University.

### 3.3. Processing of the plant material

Underground tubers (500 g) were air-dried, cut into small pieces and soaked in ethanol (~2 l) at room temperature for 24 h. The crude extract (5.8 g) obtained by filtration and evaporation was defatted with cold methanol.

### 3.4. Separation of the compounds

The defatted extract (3.1 g) was separated on Silica Gel CC into two fractions: At 1 (1.9 g, eluted by pet. ether/ether 3:1) and At 2 (0.2 g, eluted by pet. ether/ether 1:1). Fraction At 2 mainly contained fats. Most of the material was present in At 1, which was re-separated by a silica gel flash CC into four fractions (At 11, At 12, At 13a and At 13b). Fraction At 11 (620 mg, eluted by pet. ether/ether 9:1) was separated by GC/MS into **1** (17%,  $R_t$  11.22 min), **4** (10%,  $R_t$  21.92 min) and **5** (73%,  $R_t$  22.49 min). Fraction At 12 (340 mg, eluted by pet. ether/ether 4:1) according to GC/MS contained **1** (13%,  $R_t$  11.22 min), **2** (62%,  $R_t$  13.36 min) and **3** (25%,  $R_t$  14.61 min). Fraction At 13a (280 mg, eluted by pet. ether/ether 7:3) was separated by TLC (silica gel, pet. ether/ether 4:1) into **3** (52 mg,  $R_t$  0.51) and **2** (47 mg,  $R_t$  0.46). Fraction At 13b (120 mg, eluted after At 13a by the same solvent system) was a mixture of  $\beta$ -sitosterol and stigmasterol (5:1).

### 3.5. 2-Acetyl-8-methoxy-3-methyl-1-naphthol (**2**)

Yellowish gummy material; IR,  $\nu_{\max}^{\text{CHCl}_3}$ ,  $\text{cm}^{-1}$ : 3362.8 (OH), 2921.4, 2851.4 (str. CH, CH<sub>3</sub>), 1697.5 (aromatic ketone), 1633.3 (C=C), 1581.3, 1463.8, 1359.4, 1270.1, 1253.0, 1092.5, 967.4, 842.2, 758.5; <sup>1</sup>H NMR: (Table); MS,  $m/z$  (rel. int.): 230 [M]<sup>+</sup> (90.3) (corresponding to C<sub>14</sub>H<sub>14</sub>O<sub>3</sub>), 215 [M-CH<sub>3</sub>]<sup>+</sup> (100), 200 [215-CH<sub>3</sub>]<sup>+</sup> (66.7), 187 [215-CO]<sup>+</sup> (14.3), 172 [200-CO]<sup>+</sup> (3.2), 159 (9.5), 144 (11.1), 128 (17.5), 115 (38.1), 77 (7.9), 63 (14.3).

### 3.6. 2-Acetyl-1,8-dimethoxy-3-methylnaphthalene (**3**)

Yellowish gummy material; IR,  $\nu_{\max}^{\text{CHCl}_3}$ ,  $\text{cm}^{-1}$ : 2917.2, 2849.4 (str. CH, CH<sub>3</sub>), 1702.3 (aromatic ketone), 1624.0 (C=C), 1568.3, 1462.0, 1336.8, 1271.7, 1099.2, 949.7, 762.5; <sup>1</sup>H NMR: (Table); <sup>13</sup>C NMR:  $\delta$ -value (multiplicity, assignment): 206.32 (s, C=O), 155.96, 152.92 (s, C-1, C-8), 137.23, 134.55, 132.14 (s, C-2, C-4a, C-8a), 111.83 (s, C-3), 127.11, 125.15, 120.33, 105.35 (d, C-4, C-5, C-6, C-7), 63.98, 55.99 (q, 2 × OCH<sub>3</sub>), 19.04 (q, CH<sub>3</sub>); MS,  $m/z$  (rel. int.): 244 [M]<sup>+</sup> (68.3) (cor-

sponding to C<sub>15</sub>H<sub>16</sub>O<sub>3</sub>), 229 [M-CH<sub>3</sub>]<sup>+</sup> (100), 214 [229-CH<sub>3</sub>]<sup>+</sup> (9.5), 201 [229-CO]<sup>+</sup> (1.6), 186 [214-CO]<sup>+</sup> (28.6), 169 (4.8), 155 (4.8), 139 (9.5), 128 (19.1), 115 (36.5), 63 (11.0).

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Dr. M. Abdel-Mogib  
Prof. of Organic Chemistry  
King Abdulaziz University  
P.O. Box 80203  
Jeddah-21589  
Saudi Arabia  
mamdouh\_m@hotmail.com