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## Phytochemical study of Algerian *Foeniculum vulgare* Mill (Apiaceae)

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### ABSTRACT

Phytochemical investigation of the aerial parts of *Foeniculum vulgare* Mill led to isolation of two compounds from chloroform extract: graveolone **1** and 1-p-Menthene-3,6-diol **2** and two compounds from butanolic extract: Hexane-1,2,3,4,5,6-hexol (L-Iditol) **3** and Isorhamnetin-3-O- $\beta$ -glucoside **4** by the use of different chromatographic techniques. Structure elucidation of these compounds was achieved by UV, NMR spectroscopy: <sup>1</sup>H, <sup>13</sup>C-NMR, HMBC, EI-MS spectrometry and X-rays.

**Key words:** *Foeniculum vulgare*, Apiaceae, Phytochemical investigation, NMR spectroscopy, X-rays

### INTRODUCTION

*Foeniculum vulgare* Mill is a plant belonging to the Apiaceae family known as fennel it is considered as a medicinal and spice herb; it's native to southern Europe and Mediterranean area [1]. In Algeria it is cultivated for eating and for flavoring salads. Fennel is used in folk medicine for different purposes all over the spreading countries. It was considered to have diuretic, stomachic and galactogogue properties due to its volatile compounds. It was highly recommended for bronchitis and chronic cough [2]. Analgesic and antipertic activities have also been found in the fennel fruits as well as antimicrobial activity [3].

Phytochemically; the plant is typified by the presence of: phenolics compounds [4], flavonoids [5], coumarins [6], monoterpenoids [7] and essential oils [8, 9] which are the most frequently compounds investigated and showed a number of biological activities including antifungal and antioxidants [10].

The current study describes the isolation and structure elucidation of the four compounds from the aerial parts of the title plant.

### MATERIALS AND METHODS

#### Plant extract

Aerial parts of *Foeniculum vulgare* were collected in May 2005 from Ouargla, southeast of Algeria and identified by Dr Amar Zellagui, Department of Biology, University of Oum El bouaghi. A voucher specimen has been deposited at the Herbarium of Department of Biology, University of Constantine, Algeria (ZA 102).

### Extraction

Dried and powdered aerial parts of *Foeniculum vulgare* (1200g) were extracted with 70%MeOH at room temperature and combined MeOH extracts were concentrated under reduced pressure. The resultant extract (265g of dry residue) was then dissolved in H<sub>2</sub>O (1200 ml) and partitioned successively with chloroform (2g), ethyl acetate (2g) and *n*-butanol (20g). The chloroform extract was chromatographed on a silica gel column (φ3\*60 cm) using heptane and ethyl acetate from (0 to 100) as eluent, yielding 117 fractions. Fraction 45 was separated by preparative TLC using solvent system Cyclohexene-CH<sub>2</sub>Cl<sub>2</sub>-AcOEt (1:2:1) yielded compound **1** (10mg). Compound **2** was isolated from fraction 77 (25mg) as white crystal from heptane - AcOEt (50:50) (fig.1).

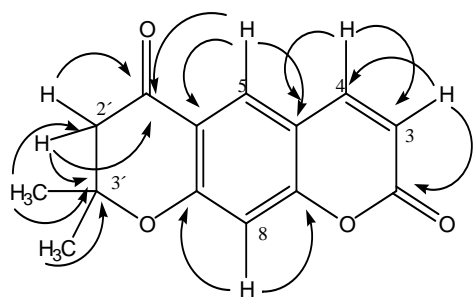
The *n*-Butanol extract was chromatographed on a silica gel column (φ4\*85 cm) eluting with CH<sub>2</sub>Cl<sub>2</sub> followed by increasing concentrations of acetone and MeOH (from 0 to 100) to yield 146 fractions. Fraction 69 to 89 (100mg) was subjected to a polyamid column chromatography for elution with a gradient system of toluene and MeOH with increasing polarity, yielded two compounds **3** (60mg) and **4** (16mg).

### RESULTS AND DISCUSSION

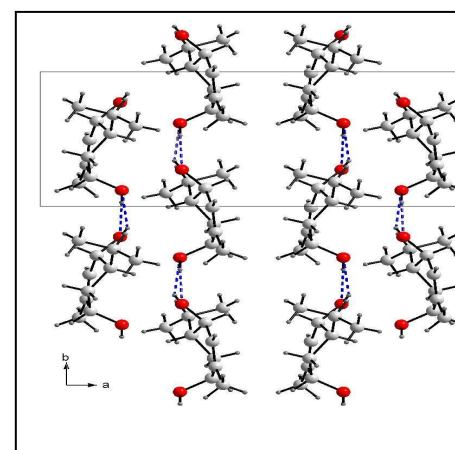
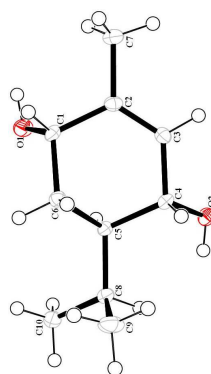
**Compound (1, Fig.1):** White powder, mp: 176-178 °C. UV (MeOH, λ<sub>max</sub>, nm): 253, 308, 329, 344. <sup>1</sup>H-NMR (400MHz, CDCl<sub>3</sub>, δ, ppm, j/Hz) : 1.52 (6H, s, 2\*CH<sub>3</sub>), 2.79 (2H, s, H-2'), 6.32 (1H, d, j=9.5Hz, H-3), 6.86 (1H, s, H-8), 7.69 (1H, d, j=9.5Hz, H-4), 8.05 (1H, s, H-5). <sup>13</sup>C-NMR (100MHz, CDCl<sub>3</sub>, δ, ppm) : 27.12(C-4', C-5'), 49.05(C-2'), 81.16(C-3'), 106.02(C-8), 113.71(C-6), 115.01(C-3), 118.00(C-10), 127.60(C-5), 143.56(C-4), 159.49(C-9), 160.33(C-7), 162.61(C-2), 191.25(C-1'). EI-MS<sup>+</sup> (m/z): 244 [M<sup>+</sup>], 229 [M<sup>+</sup>-CH<sub>3</sub>], 201 [M<sup>+</sup>-CH<sub>3</sub>-CO], 189 [M<sup>+</sup>-C<sub>4</sub>H<sub>7</sub>]. This compound was characterized as **8,8-dimethyl-2H,6H,7H,8H-pyrano[3,2-g]chromene-2,6-dione(Graveolone)**.

**Compound (2, Fig.2):** White crystal, mp: 164-165 °C. <sup>1</sup>H-NMR (300MHz, CD<sub>3</sub>OD, δ, ppm, j/Hz): 5.39(1H, s, H-2), 3.84(1H, s, H-6), 3.76(1H, t, j=9, H-3), 3.21(s, OH-6 and OH-3), 2.02(1H, dsp, j=13, 4, H-8), 1.68(3H, s, CH<sub>3</sub>-7), 1.60(1H, dt, j=13, 4, H-5β), 1.51(1H, ddt, j=12, 9, 3, H-4), 1.30(1H, td, j=13,4, H-5α), 0.92(3H, d, j=7, CH<sub>3</sub>-9), 0.72(3H, d, j=7, CH<sub>3</sub>-10). <sup>13</sup>C-NMR (75MHz, CD<sub>3</sub>OD, δ, ppm): 136.39(C-1), 130.00(C-2), 68.91(C-3), 67.37(C-6), 41.79(C-4), 29.84(C-5), 25.96(C-8), 20.38(C-7), 19.67(C-9), 16.02(C-10). This compound was characterized as (**1R, 4S, 5S**) **5-isopropyl-2-methylcyclohex-2-ene-1,4diol (1-p-Menthene-3,6-diol)**

**Compound (3):** White powder, mp: 161-164°C. <sup>1</sup>H-NMR (250MHz, D<sub>2</sub>O, δ, ppm): 3.42-3.75. <sup>13</sup>C-NMR (62.5MHz D<sub>2</sub>O, δ, ppm): 70.69(C-2, C-5), 69.12(C-3, C-4), 63.12(C-1, C-6). EI-MS<sup>-</sup> (m/z): 181.2[M-H], 182.2[M<sup>+</sup>]. This compound was characterized as **Hexane-1,2,3,4,5,6-hexol (L-Iditol)**.



HMBC correlation of the compound 1



ORTEP drawing of compound 2

Figure1. Chemical structure of compounds 1 and 2.

**Compound (4):** Yellow powder, mp: 184-186°C. UV(MeOH, λ<sub>max</sub>, nm): 357, 300sh, 255; +NaOH: 404, 330, 273; +AlCl<sub>3</sub>: 364, 257; AlCl<sub>3</sub>+HCl: 358, 303, 267; +NaOAc: 383, 323sh, 273; NaOAc+H<sub>3</sub>BO<sub>3</sub>: 366, 267. <sup>1</sup>H-NMR (250MHz, DMSO, δ, ppm, j/Hz): 8.39(1H, d, j=2Hz, H-2'), 7.45(1H, dd, j=8.4, 2Hz, H-6'), 6.35(1H, d, j=8.4Hz, H-5'), 6.20(1H, d, j=2Hz, H-8); 6.08(1H, d, j=2Hz, H-6); 5.60(1H, d, j=7.5Hz, H-1''), 3.95(3H, s, 3-OCH<sub>3</sub>). <sup>13</sup>C-NMR (DMSO, 62.5MHz, δ, ppm) : 177.68(C-4), 172.23(C-7), 164.80(C-5), 161.46(C-9), 156.72(C-2), 149.49(C-3),

147.17(C-4'), 133.14(C-3), 122.07(C-6'), 121.64(C-1'), 115.36(C-5'), 114.63(C-2'), 104.04(C-10), 101.08(C-1''), 98.87(C-6), 94.12(C-8), 76.70(C-5''), 76.7(C-3''), 74.40(C-2''), 72.40(C-4''), 70.65(C-6''), 56.10(3-OCH<sub>3</sub>). EI-MS<sup>+</sup> (m/z): 501.06[M+Na]<sup>+</sup>, 502.06 [M+H+Na]<sup>+</sup>, 317.06[M+H-glucose]<sup>+</sup>. This compound was characterized as *Isorhamnetin-3-O-β-glucoside*.

### CONCLUSION

The four known compounds were also established by spectroscopic analysis and by aid of Literature data [11-12-13]. Although compound namely Graveolone is known in other genera, this is the first report of isolation of this compound in *Foeniculum vulgare*. Thus, this finding will be helpful for the chemotaxonomic profile of this species for further investigations.

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