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Two New Compounds from *Melanosciadum pimpinelloideum* H. Boiss

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Abstract: Two new compounds, melanochromone and 2-ethoxyl-2-(4-hydroxyphenyl)ethanol, were isolated from the whole plants of *Melanosoiadum pimpinelloideum* H. Boiss. The known compounds isolated were 1-(4-hydroxyphenyl)-1,2-ethanediol, tymine, cimifugin, umtatin, bergenin, daucosterol and stigmasterol. Their structures were determined on the basis of spectral data.

Keywords: *Melanosciadum pimpinelloidum,* melanochromone, 2-ethoxyl-2-(4-hydroxyphenyl) ethanol.

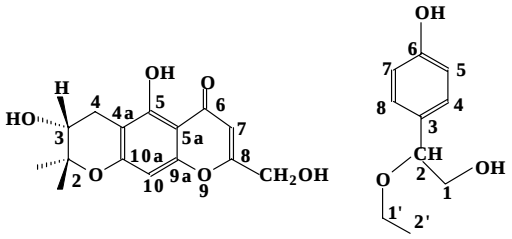
Melanosciadum pimpinelloideum H. Boiss (Umbelliferae), an indigenous plant，is the unique representative of species *Melanosciadum*[1]. Anomalin and 3′-angeloyl-4′-hydroxy-*trans*-khellactone were isolated from this plant[2]. In this investigation, from the whole plants two new compounds, melanochromone **1** and 2-ethoxyl-2-(4-hydroxyphenyl)ethanol **2** were isolated with known compounds 1-(4-hydroxyphenyl)-1,2-ethanediol **3**[3], tymine (5-methyluracil) **4**[4], cimifugin **5**[5], umtatin **6**[5], bergenin **7**[6], daucosterol **8**[7] and stigmasterol **9**[8].

Melanochromone **1** was obtained as yellow cubic crystals. Its EIMS gave the molecular ion peak at *m/z* 292. From its ^{1}H NMR spectrum, two methyl groups at δ 1.50 (3H, s) and 1.55 (3H, s) and a hydroxymethyl group at δ 4.64 (2H, s) could be recognized. According to the ^{1}H NMR signals at δ 3.11 and 2.81 (each 1H,dd, J = 5.4, 1.8 Hz, 4-H) and δ 4.00 (1H, q, J = 5.4 Hz, 3-H) as well as the ^{13}C NMR signals at δ 61.7 (C-3) and 26.3 (C-4), the moiety –CH (OH)-CH_2- was resumed. Its UV absorption at λ_{max} 295, 262 and 242 nm resembled those of 3, 4-dihydro-2H, 3H-benzo[1,2-b: 5,4-b′]dipyran-6-one[9]. The bathochromic shift from λ_{max} 295 to 338 nm in its UV spectrum after adding $AlCl_3$ suggested the presence of 5-OH. Nine of the fifteen signals observed in ^{13}C NMR spectrum appear over δ 95 including a signal at δ 184.5 for conjugated carbonyl group, confirmed a benzopyrane-4-one moiety. Two signals in ^{1}H NMR at δ 6.52 and 6.46 (each 1H, s) could be assigned to 7-H and 10-H, respectively. A quaternary C-atom resonates at δ 80.3 (C-2). Thus, the structure of **1** could be determined as illustrated in **Figure 1**.

Compound **2** was obtained as colorless cubic crystals. Its EIMS spectrum gave a $[M]^+$ at *m/z* 182. From its IR spectrum, hydroxyl group (3256 cm^{-1}) and aromatic rings (1611, 1579, 1514 and 1450 cm^{-1}) could be concluded. In its ^{1}H NMR spectrum, the signals at δ 7.14 and 6.79 (each 2H, d, J = 7.5 Hz) showed a 1, 4- substituted phenyl ring. The signals at δ 3.33 (2H, d, J = 2.3 Hz) and δ 1.10 (3H, t, J = 2.3 Hz) in ^{1}H NMR, and the ^{13}C NMR signals at δ 64.9 and 16.0 demonstrated the presence of ethoxyl group.

The ^{13}C NMR signals at δ 84.0 (d) and 68.9 (t) indicated the presence of moiety -O-CH-CH_2-O-. On the basis of the evidence mentioned above, compound **2** could be determined as 2-ethoxyl-2-(4-hydroxyphenyl) ethanol.

Melanochromone 1 Yellow cubic crystals. m.p. 122.5-124°C (MeOH). $[\alpha]_D^{22}$ –8.8 (*c* 0.91, MeOH). UV λ_{max}^{MeOH}(log ε) nm: 242 (4.25), 262 (4.35) and 295 (4.00). UV $\lambda_{max}^{MeOH+AlCl_3}$ nm: 265, 338. IRν cm^{-1}: 3394 (-OH), 1655 (C=O), 1624, 1573 and 1483



1 **2**

(aromatic). EIMS *m/z* (rel. int.): 292 ($[M]^+$, 38), 259 (5), 233 (10) and 221 (100). ^{1}H NMR (CD_3OD, 400 MHz): δ 4.00 (1H, q, *J* = 5.4 Hz, 3-H), 3.11 and 2.81 (each 1H, dd, *J* = 5.4, 1.8 Hz, 4-H), 6.52 (1H, s, 7-H), 6.46 (1H, s, 10-H), 1.50 and 1.55 (each 3H, s, 1′- and 2′-Me), 4.64 (2H, s, -C<u>H</u>$_2$OH). ^{13}C NMR (CD_3OD, 100 MHz): δ80.3 (C-2), 61.7 (C-3), 26.3 (C-4), 105.6 (C-4a), 161.40 (C-5), 105.60 (C-5a), 184.5 (C-6), 106.7 (C-7), 172.0 (C-8), 157.7 (C-9a), 96.1 (C-10), 160.7 (C-10a), 21.8 (C-1′), 26.0 (C-2′), 69.6 (-CH_2OH).

2-Ethoxy-2-(4-hydroxyphenyl)ethanol 2 Colorless cubic crystals. m.p. 99-100 °C (acetone). $[\alpha]_D^{22}$ -0.5 (*c* 0.56, acetone). UV λ_{max} nm: 221 and 275. IRν cm^{-1}: 3256 (-OH), 1611, 1579 and 1514 (phenyl). EIMS *m/z* (rel. int.): 182 ($[M]^+$, 5), 151 (100), 123 (100), 107 (12), 95 (40), 65 (15) and 39 (15). ^{1}H NMR (CD_3COCD_3, 400 MHz): δ3.38 (2H, d, *J* = 4.1 Hz, 1-H), 4.25 (1H, t, *J* = 4.1 Hz, 2-H), 6.79 (2H, d, *J* = 7.5 Hz, 4- and 8-H), 7.14 (2H, d, *J* = 7.5 Hz, 5- and 7-H), 3.33 (2H, q, *J* = 2.3 Hz, 1'-H), 1.10 (3H, t, *J* = 2.3 Hz, 2'-H). ^{13}C NMR (CD_3COCD_3, 100 MHz): δ68.2 (C-1), 84.0 (C-2), 132.0 (C-3), 116.2 (C-4, C-8), 129.2 (C-5, C-7), 158.2 (C-6), 64.9 (C-1'), 16.0 (C-2').

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