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MINOR PHENOLICS OF *APIUM GRAVEOLENS* SEEDS

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Key Word Index—*Apium graveolens*; Umbelliferae; seeds; myristicic acid; 8-hydroxy-5-methoxypsoralen; umbelliferone.

In continuation of our work [1] on *Apium graveolens* seeds, 3 more compounds have been isolated from the Et_2O extract. These have been identified as 3-methoxy-4,5-methylenedioxybenzoic acid (myristicic acid), 8-hydroxy-5-methoxypsoralen and umbelliferone. This is the first report of the natural occurrence of myristicic acid. The structure 8-hydroxy-5-methoxypsoralen assigned to the second compound has been confirmed by synthesis from isopimpinellin. This is the first report of its presence in *A. graveolens* but it has recently been isolated from *Angelica archangelica* [2].

EXPERIMENTAL

Isolation. The Et_2O extract was chromatographed on Si gel (400 g) using C_6H_6 as eluent. Three fractions were collected, which according to TLC (Si gel; $CHCl_3$–MeOH, 23:2), each showed the presence of one major spot. Crystallization of these fractions from EtOAc–petrol yielded compounds E_3, E_4 and E_5 respectively.

Identification. Compound E_3, colourless needles (50 mg), mp 208–10°; R_f 0.66 ($CHCl_3$–MeOH, 1:3); 0.57 (MeOH–EtOAc, 3:2); (Found: M^+ 196; C, 55.2; H, 3.9. $C_9H_8O_5$ requires: C, 55.1; H, 4.1 %). UV λ_{max}^{MeOH} nm log (ε) 265 (3.8), 310 (2.9), 340 (1.8); IR ν^{KBr} cm^{-1}: 1675, 1640, 1430, 1325 and 1040; PMR (DMSO-d_6, δ); 3.95 (*s*, 3H, $-OCH_3$), 6.26 (*s*, 2H, $-OCH_2O-$), 7.27 and 7.42 (two *d*, *J* = 2 Hz, 1H each, two aromatic protons). It gave a positive sulphuric acid–gallic acid test indicating the presence of a methylenedioxy group. Methylation with CH_2N_2 gave the ester, mp 93–4°; (Found: C, 57.4; H, 4.9. $C_{10}H_{10}O_5$ requires: C, 57.1; H, 4.8 %); UV λ_{max}^{MeOH} nm log (ε) 250 (3.2), 280 (3.5), 350 (2.8); IR ν^{KBr} cm^{-1}: 1700, 1632, 1418, 1317 and 1034. Compound E_3 was identical with an authentic sample of myristicic acid [3].

Compound E_4, yellow needles (150 mg) mp 218°; (Found: C, 62.4; H, 3.9. $C_{12}H_8O_5$ requires: C, 62.0; H, 3.5 %); UV λ_{max}^{MeOH} nm log (ε) 275 (4.4), 320 (4.1); IR ν^{KBr} cm^{-1}: 3340, 1685, 1630, 1086 and 887. The acetyl derivative (Ac_2O/Py) crystallized from EtOAc–petrol as colourless needles, mp 187°; (Found: M^- 274; C, 61.1; H, 3.5. $C_{14}H_{10}O_6$ requires: C, 61.3; H, 3.7 %); UV λ_{max}^{MeOH} nm log (ε) 245 (4.3), 260 (4.5), 310 (4.1); IR ν^{KBr} cm^{-1}: 1700, 1625, 1267, 1086 and 892; PMR ($CDCl_3$, δ); 2.5 (*s*, 3H, $-OCOCH_3$); 4.4 (*s*, 3H, $-OCH_3$); 6.4 (*d*, *J* = 10 Hz, 1H, coumarin 3); 7.3 (*d*, *J* = 2 Hz, 1H furan); 7.8 (*d*, *J* = 2 Hz, 1H furan); 8.4 (*d*, *J* = 10 Hz, 1H, coumarin 4). E_4 formed a Me ether (CH_2N_2), mp 150°; (Found: M^+ 246; C, 63.7; H, 4.5. $C_{13}H_{10}O_5$ requires: C, 63.4; H, 4.1 %); UV λ_{max}^{MeOH} nm log (ε) 240 (3.9), 265 (4.1), 310 (3.9); IR ν^{KBr} cm^{-1}: 1710, 1595, 1340, 1085 and 890; identical (mmp, UV, IR) with isopimpinellin. Compound E_4 is, therefore, 8-hydroxy-5-methoxypsoralen.

Synthesis of 5,8-dihydroxypsoralen. A soln of isopimpinellin (250 mg) in HOAc (10 ml) was treated for 1 hr with conc HNO_3 (1.19 d, 3 ml). The precipitated quinone was filtered, washed with H_2O and dried (P_2O_5). It crystallized from $CHCl_3$ as an orange coloured powder (125 mg) mp 265°; (Found: C, 61.3; H, 2.2. $C_{11}H_4O_5$ requires; C, 61.1; H, 1.9 %); UV λ_{max}^{MeOH} nm log (ε) 270 (4.0), 285 sh (4.0), 315 (3.8), 350 (3.1); IR ν^{KBr} cm^{-1}: 1735, 1640, 1560, 970 and 850.

The quinone (100 mg) in EtOH (15 ml) was reduced by passing SO_2 gas. The pale yellow soln was evapd, the residue washed with H_2O and dried (P_2O_5). The quinol crystallized from MeOH–$CHCl_3$ as pale yellow needles (70 mg) mp 275°; (Found: C, 60.4; H, 3.0. $C_{11}H_6O_5$ requires: C, 60.6; H, 2.8 %); UV λ_{max}^{MeOH} nm log (ε) 280 (3.9), 315 (3.7), 350 (3.2); IR ν^{KBr} cm^{-1}: 3400, 1670, 1612, 1095 and 862. The quinol diacetate (Ac_2O/Py) crystallized from $CHCl_3$–petrol as colourless needles (30 mg), mp 213–4°; (Found: C, 59.9; H, 3.7. $C_{15}H_{10}O_7$ requires: C, 59.6; H, 3.4 %); UV λ_{max}^{MeOH} nm log (ε) 245 (3.8), 295 (3.5), 350 (2.9); IR ν^{KBr} cm^{-1}: 1715, 1630, 1585, 987 and 877; PMR ($CDCl_3$, δ): 2.6 (*s*, 6H, 2 × $-OCOCH_3$); 6.67 (*d*, *J* = 10 Hz, 1H, coumarin 3); 7.02 (*d*, *J* = 2 Hz, 1H furan); 8.02 (*d*, *J* = 2 Hz, 1H furan); 8.2 (*d*, *J* = 10 Hz, 1H, coumarin 4).

Synthesis of 8-hydroxy-5-methoxypsoralen. The quinol (50 mg) in dry Me_2CO (20 ml) was selectively methylated with Me_2SO_4 (0.3 ml, 0.9 mol) and $NaHCO_3$ (1 g) [4, 5]. TLC examination of the crude product showed the presence of one major product. It was purified by preparative-TLC (Si gel, MeOH–$CHCl_3$, 3:97). It crystallized as yellow needles (20 mg), mp 217–8°; (Found: C, 62.3; H, 3.8. $C_{12}H_8O_5$ requires: C, 62.1; H, 3.5 %). It was identical (mmp, UV, IR) with a natural sample of compound E_4.

Compound E_5 was identified as umbelliferone on direct comparison with an authentic sample.

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