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SECONDARY CONSTITUENTS FROM *Carum montanum*

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In continuation of the systematic chemical studies of endemic algerian plants [1, 2], we present here the continuation of our research on the chemical composition of the aerial part of *Carum montanum*. The present paper deals with the isolation and characterization of six substances belonging to various classes of compounds, specifically four furanocoumarins in which one is a glucoside, one is a coumarin, and two are aromatic compounds. Compounds **1–6** were identified by GC-MS analysis and (UV, MS, ^{1}H NMR, and ^{13}C NMR spectroscopy) as: bergapten **1**, isobergapten **2,** osthol **3,** nothoapiole **4**, isopimpinellin **5**, and 8-hydroxy-5-*O*-β-D-glucosylpsoralen **6**.

Leaves of *C. montanum* [3] were collected from Megress Mountain (Eastern Algeria) at 1500 m above sea level during June 2004 and identified by Dr. H. Laouer. A voucher specimen (B-6306) has been deposited in the Museum d'Histoire Naturelle of Nice (France).

The air-dried aerial parts of *C. montanum* (300 g) were pulverized and extracted with methanol (75%) three times. The combined extracts were evaporated in vacuo, suspended in water, and partitioned with EtOAc and *n*-butanol. The EtOAc extract (3.3 g) was chromatographed on a silica gel column by gradient elution with CH_2Cl_2 to give eight fractions (fr. 1–8). Each fraction was then subjected to repeated chromatography on silica gel by PTLC to yield compounds **1** (7.3 mg), **2** (6 mg) , **3** (8 mg), **4** (1.7 mg), and **5** (21 mg), The *n*-BuOH extract (8.9 g) was chromatographed on a polyamid SC6 column by gradient elution with toluene–MeOH to give **6** (20 mg). The structures of the pure compounds were proved using UV, ^{1}H NMR, ^{13}C NMR, DIC/NH_3 and ES/MS analytical methods. Multiple-pulse 2D NMR experiments (^{1}H–^{1}H COSY, ^{1}H–^{1}H NOESY, ^{13}C–^{1}H HETCOR, and ^{13}C–^{1}H COLOC) were used for the structure elucidation of compounds **1–2** and **4–6**.

Compound 1, $C_{12}H_8O_4$, mp 190°C, *m/z* 216, identified as bergapten [4–6].

Compound 2, $C_{12}H_8O_4$, mp 226–228°C, *m/z* 216 (M^+), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 8.10 (1H, d, J = 9.8, H-4), 7.06 (1H, s, H-6), 7.52 (1H, d, J = 2.2, H-9), 6.95 (1H, d, J = 2.2, H-10), 6.21 (1H, d, J = 9.8, H-3), 4.20 (3H, s, OMe-5). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 61.22 (OMe-5), 95.21 (C-6), 112.91 (C-3), 105.45 (C-4a), 105.50 (C-10), 138.50 (C-8a), 139.70 (C-4), 145.19 (C-9), 156.11 (C-5), 156.46 (C-7), 160.9 (C-2) identified as isobergapten [7, 8].

Compound 3, $C_{15}H_{16}O_3$, mp 82–84°C, *m/z* 244, identified as osthol [7].

Compound 4, $C_{12}H_{15}O_5$, oil, *m/z* 252 (M^+), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 5.90 (1H, s, H-2′), 5.82 (2H, s, H-2), 4.92 (2H, m, H-3′), 3.87 (3H, s, OMe-4), 3.81 (3H, s, OMe-7), 3.69 (3H, s, OMe-5), 3.25 (1H, dt, J = 6.0, 1.5, 1.5, H-1′). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 100.17 (C-2), 113.35 (C-6), 132.2 (C-1), 133.4 (C-3), 135.53 (C-4), 136.6 (C-7), 143.9 (C-5) identified as nothoapiole [9, 10].

Compound 5, $C_{13}H_{10}O_5$, mp 151–153°C, *m/z* 246 (M^+), ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 8.07 (1H, d, J = 9.8, H-4), 7.56 (1H, d, J = 2.2, H-9), 6.93 (1H, d, J = 2.1, H-10), 6.20 (1H, d, J = 9.8, H-3), 4.09 (3H, s, OMe-5), 4.07 (3H, s, OMe-8). ^{13}C NMR (75 MHz, $CDCl_3$, δ, ppm): 61.22 (OMe-5), 62.13 (OMe-8), 105.20 (C-10), 108.01 (C-4a), 113.25 (C-3), 115.18 (C-6), 128.50 (C-8), 139.82 (C-4), 144.08 (C-5), 144.69 (C-8a), 145.53 (C-9), 150.41 (C-7), 160.9 (C-2) identified as isopimpinellin [7, 8, 11].

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Compound 6, $C_{18}H_{16}O_{10}$, *m/z* 380 (M^+), ^{1}H NMR (DMSO-d_6, 300 MHz, δ, ppm, J/Hz): 8.50 (1H, d, J = 9.9, H-4), 8.00 (1H, d, J = 2.1, H-9), 7.31 (1H, d, J = 2.1, H-10), 6.36 (1H, d, J = 9.9, H-3), 4.70 (H, d, J = 7.74, H-1′ of glucose), 3.25–3.70 (6H of the glucose). ^{13}C NMR (75 MHz, DMSO-d_6, δ, ppm): 60.81 (Glc-6′), 69.61 (Glc-4′), 73.75 (Glc-2′), 76.24 (Glc-3′), 77.17 (Glc-5′), 105.07 (Glc-1′), 105.71(C-10), 108.86 (C-4a), 112.65 (C-3), 117.36 (C-6), 126.64 (C-8), 138.58 (C-4), 139.15 (C-8a), 140.73 (C-5), 146.25 (C-7), 146.36 (C-9), 159.93 (C-2). Identified as 8-hydroxy-5-*O*-β-D-glucosylpsoralen, originally isolated from the roots of *Heracleum rapula* Franch [12].

To our knowledge, this is the first report on the occurrence of compounds **1**, **2** and **4**, **5** in the aerial parts of *C. montanum* and the first report on the isolation of compounds **3** and **6** from the genus *Carum*; it is also the first report on the ^{13}C NMR values for compounds **2** and **4**.

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