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A NEW NATURAL METHOXYFUROCOUMARIN FROM *Heracleum pastinacifolium*

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Isobergapten, pimpinellin, isopimpinellin, osthole, and a new natural monomethoxyfurocoumarin were isolated and identified from roots of Heracleum pastinacifolium.

Keywords: furocoumarin, *Heracleum pastinacifolium*, NMR spectrum, chemical shift, spin–spin coupling constant.

We reported earlier [1] on coumarin derivatives from *Heracleum pastinacifolium* C. Koch. (Apiaceae). In continuation of research on plants of the genus *Heracleum*, we studied roots of *H. pastinacifolium* collected during fruiting near Lake Gek-Gel in Gek-Gel Nature Reserve, Azerbaijan Republic, on August 27, 2008. Plant material collected from this site was identified as *H. pastinacifolium* by I. I. Karyagin [2].

Total extracted substances obtained by extraction of ground air-dried roots with acetone were separated over a column of Al_2O_3 with elution by hexane, hexane:benzene in various ratios, benzene, benzene:$CHCl_3$, and pure $CHCl_3$. This isolated five coumarin-type compounds: $C_{12}H_8O_4$, mp 223–224°C (**1**, ν_{max} 1751, 1630, 1610 cm^{-1}); $C_{12}H_8O_4$, mp 172–174°C (**2**, ν_{max} 1730, 1630, 1600); $C_{13}H_{10}O_5$, mp 117–119°C (**3**, ν_{max} 1745, 1630, 1585, 1547); $C_{13}H_{10}O_5$, mp 149–151°C (**4**, ν_{max} 1755, 1732, 1600, 1558); and $C_{15}H_{16}O_3$, mp 84–85°C (**5**, ν_{max} 1730, 1620, 1565).

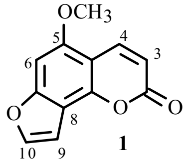
Compounds **1** and **3**–**5** were identified by direct comparison of IR spectra as isobergapten, pimpinellin, isopimpinellin, and osthole, respectively [3–5].

The PMR spectrum of **2** had a 3H singlet at 4.00 ppm (CH_3O) and 1H doublets at 6.35 ppm (J = 9.9 Hz, H-3), 7.98 (J = 9.9 Hz, H-4), 7.10 (1H, s), 7.16 (1H, d, J = 2.3 Hz), and 7.94 (1H, d, J = 2.3 Hz) that belonged to protons of a methoxyfurocoumarin.

The ^{13}C NMR spectrum taken with full spin–spin decoupling showed 12 resonances corresponding to 12 C atoms of the studied molecule. The ^{13}C DEPT-135 spectrum had six resonances (54.0, 103.0, 104.0, 112.0, 145.0, 147.0 ppm) for protonated C atoms, of which five according to ^{13}C DEPT-90 NMR (104.0, 105.0, 114.0, 145.5, 147.5 ppm) belonged to olefinic (CH=) C atoms.

Thus, a study of these ^{13}C NMR and ^{13}C DEPT-135 and DEPT-90 spectra found easily that **2** was a methoxyfurocoumarin.

The known methoxyfurocoumarins isobergapten (**1**), bergapten (**6**), xanthotoxin (**7**), sphondin (**8**), and allobergapten (**9**) (obtained during the synthesis of bergapten) [15] (Table 1) differ in the placement of the methoxyl and the furan ring.



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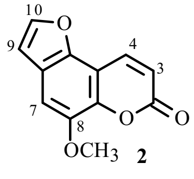

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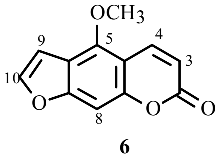

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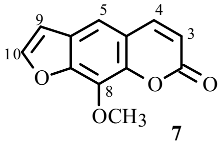

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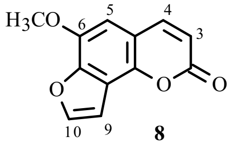

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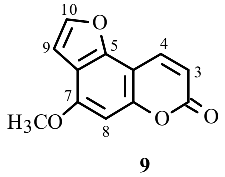

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TABLE 1. PMR Spectra of Monomethoxyfurocoumarins **2**, **6**, **7**, **8** (δ, ppm, J/Hz) [6]

C atom	**2**	**6**	**7**	**8**
3	6.35 (d, J = 9.9)	6.26 (d, J = 10.0)	6.35 (d, J = 10.0)	6.39 (d, J = 9.7)
4	7.98 (d, J = 9.9)	8.13 (d, J = 10.0)	7.77 (d, J = 10.0)	7.76 (d, J = 9.7)
5			7.35 s	6.77 s
7	7.10 s			
8		7.10 s		
9	7.16 (d, J = 2.3)	7.02 (d, J = 2.3)	6.82 (d, J = 2.3)	7.12 (d, J = 2.3)
10	7.94 (d, J = 2.3)	7.58 (d, J = 2.3)	7.64 (d, J = 2.3)	7.67 (d, J = 2.3)
5-OCH_3		4.26 s		
6-OCH_3				4.03 s
8-OCH_3	4.0 s		4.28 s	

IR and PMR spectra of **6**, **7**, and **8** did not agree with those of **2**. Therefore, the studied compound had the structure 7-methoxy-8*H*-furo[2,3-*h*]-1-benzopyran-2-one (allobergapten) [5] or 8-methoxy-8*H*-furo[2,3-*h*]-1-benzopyran-2-one (**2**). The latter structure (**2**) was more preferred.

EXPERIMENTAL

IR spectra were recorded in mineral oil on a UR-20 spectrophotometer. PMR and ^{13}C NMR spectra were taken in deuterated acetone on a Bruker 300 spectrometer at operating frequency 300 MHz for ^1H and 75 MHz for ^{13}C. Chemical shifts were determined on the δ-scale relative to TMS internal standard. Melting points were measured on a Boetius stage. The purity of compounds was established on Silufol UV-254 chromatographic plates.

Total Extracted Substances. Ground air-dried roots of *H. pastinacifolium* (300 g) were extracted with acetone (3×, each time for 3 d). The extracts were filtered and evaporated to afford total extracted dark-brown substances (32.3 g, 10.76% yield).

Isolation of Coumarin Derivatives. Total extracted substances (30 g) were chromatographed over a column of Al_2O_3 (neutral, III-IV activity) (h = 90, d = 3.5 cm) with elution by hexane, hexane:benzene (9:1, 8:2, 7:3, 6:4, 1:1, 1:2, 1:3, 1:4), benzene, benzene:$CHCl_3$ (4:1, 3:2, 1:1), and $CHCl_3$. The volume of each fraction was 100 mL.

Fraction 10, which eluted with hexane:benzene (3:2) contained osthole; fraction 12, pimpinellin; fractions 15–16, which eluted with hexane:benzene (1:1), isobergapten; fraction 22, isopimpinellin [3].

Compound **2** was isolated from fractions 32–35, which eluted with hexane:benzene (1:2), $C_{12}H_8O_4$, mp 172–174°C, ν_{max} 1730, 1630, 1600 cm^{-1}. Table 1 presents the NMR data.

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