

A NEW PSORALENIC METHOXYFUROCUMARIN FROM FRUIT OF *Heracleum transcaucasicum*

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A new methoxyfurocoumarin of formula C₁₂H₈O₄ with mp 180–182°C was isolated from ripe fruit of Heracleum transcaucasicum. Its structure was established using spectral data (IR, PMR, ¹³C NMR, DEPT 135).

Keywords: *Heracleum transcaucasicum*, psoralen, methoxyfurocoumarin, IR and NMR spectroscopy, chemical shift, spin–spin coupling constant.

Coumarins from roots of *Heracleum transcaucasicum* Manden. ex Grossh. collected in Molla-Gasanly, Dashkasan Region, Republic of Azerbaijan, were recently reported [1].

Herein we present results from a structural study of a new methoxyfurocoumarin isolated from ripe fruit of this plant.

The studied compound had formula C₁₂H₈O₄ and mp 180–182°C (aqueous EtOH). Its IR spectrum contained absorption bands for a δ-lactone carbonyl (1710 cm⁻¹) and a –C=C aromatic system (1600). There was no hydroxyl band.

The ¹³C NMR spectrum taken with full suppression of spin–spin coupling exhibited 12 singlets (60.0, 93.5, 106.0, 112.0, 140.0, 144.5, 146.0, 148.5, 150.0, 152.0, 158.0, 160.0 ppm) of which according to the DEPT 90 ¹³C NMR spectrum 6 belonged to protonated C atoms including 1 methyl (60.0) and 5 aromatic (93.5, 106.0, 112.0, 140.0, 146.0) C atoms. Therefore, the remaining 6 resonances observed in the ¹³C NMR spectrum of the compound (144.5, 148.5, 150.0, 152.0, 158.0, 160.0) belonged to unprotonated C atoms.

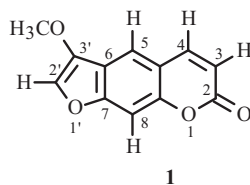
A comparison of the spectral data with those of known furocoumarins showed that the studied compound was a new linear methoxyfurocoumarin for which we proposed the name furomethoxyheraclin.

The PMR spectrum showed resonances characteristic of psoralenic monomethoxyfurocoumarins. Thus, the PMR spectrum contained resonances of methoxyl at 4.25 ppm (3H, s) and five 1H resonances at 6.30 (1H, d, J = 10 Hz, H-3), 8.15 (1H, d, J = 10 Hz, H-4), 7.30 (1H, s, H-5), 7.40 (1H, s, H-8), and 8.00 ppm (1H, s, H-2' or H-3'). A multiplet of resonances proved that the studied compound was a linear furocoumarin (psoralen group).

If the methoxyl was located on C-5, we had a compound identical to bergapten; on C-8, xanthotoxin. However, the IR and PMR spectra of the compound did not agree with that of bergapten or xanthotoxin [2, 3]. On the other hand, the observation at weak field in the PMR spectrum of three 1H singlets (7.30, 7.40, 8.00 ppm) and two 1H doublets (6.30, J = 10 Hz; 8.15, J = 10 Hz) also indicated that the compound was different from bergapten or xanthotoxin [2]. The NMR spectra of bergapten and xanthotoxin are known to exhibit at weak field (in contrast with the spectrum of the studied compound) doublets for H-3 and H-4 in addition to 1H resonances at 7.10 (s, H-8), 7.02 (d, J = 2.3 Hz, H-3'), 7.58 (d, J = 2.3 Hz, H-2'), and 7.35 (s, H-5), 6.82 (d, J = 2.3 Hz, H-3'), 7.64 (d, J = 2.3 Hz, H-2') [2, 4], respectively.

Thus, all obtained data indicated unambiguously that the studied compound was different from bergapten and xanthotoxin. Therefore, the methoxyl could be located on C-2' or C-3', as indicated by the doublets for the furan protons of bergapten and xanthotoxin and the singlet (8.00 ppm) of the only proton (H-2') of the studied compound. Judging from these data, the methoxyl in furomethoxyheraclin could be located on C-3'. The methoxyl could not be located on C-2' because any group (hydroxyl, ester, etc.) in linear furocoumarins isolated until now from plants, e.g., deltoin, peucedanin, pranchimigin, athamantin, etc., is bonded through an isopropyl group located on the furan C-2' [4, 5].

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Based on the aforementioned, the most probable structure of furomethoxyheraclin was proposed as structure **1**.

EXPERIMENTAL

IR spectra were recorded in mineral oil on a UR-20 spectrophotometer; PMR and ^{13}C NMR spectra, in DMSO- d_6 on a Bruker 300 spectrometer at operating frequency 300 MHz for ^1H and 75 MHz for ^{13}C . Chemical shifts were determined relative to TMS internal standard on the δ -scale. Melting points were determined on a Boetius stage. The purity of compounds was established on Silufol UV 254 chromatography plates.

Isolation of Total Extracted Substances. Finely ground ripe fruit of *H. transcaucasicum* (278.0 g) was extracted (3 \times , each for 3 d) by acetone. The extracts were filtered and evaporated to afford the dark-brown total extracted substances (24.7 g) in 8.88% yield.

Isolation of Furomethoxyheraclin. The liquid part of the total extracted substances was separated from the resinous solid part. The resinous part (10.8 g) was chromatographed over a column of Al_2O_3 (neutral, Brockmann activity III-IV, $h = 30$, $d = 3$ cm). Fractions (50 mL) were collected upon elution by hexane, hexane:benzene (4:1, 3:2, 1:1, 1:2, 1:3, 1:4), benzene, a benzene: CHCl_3 gradient (4:1, 1:1, 1:2), and CHCl_3 . The tenth fraction obtained upon elution by benzene consisted of a mixture of two compounds and was rechromatographed over a column of Al_2O_3 ($h = 20$, $d = 1.5$ cm) using benzene. Fractions (30 mL) afforded the pure crystalline compound $\text{C}_{12}\text{H}_8\text{O}_4$, mp 180–182°C.

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