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OCCURRENCE OF COUMARINS IN *Seseli hartvigii* GROWING IN TURKEY

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Seseli is an old Greek name mentioned by Hippocrates for certain members of the Umbelliferae (Apiaceae) family [1]. The genus *Seseli* L. is represented by 12 taxa (11 species and 1 subspecies) in the *Flora of Turkey*, of which 4, including the title species, are native to the region [2–5]. Some other *Seseli* species have been used in Turkey. For example, the fruits of *S. tortuosum* are used as an emmenagogue and anti-flatulence in Turkish folk medicine [6], while the leaves of *S. libanotis* (Kelemkesir or Kelemenkesir in Turkish) are consumed as a vegetable in eastern Turkey [7].

Seseli hartvigii Parolly & Nordt (Umbelliferae), which is a monocarpic and perennial plant, is distributed in southern Anatolia as an endemic Turkish species [3, 5]. There is no ethnobotanical report for *Seseli hartvigii*.

Various phytochemical studies carried out on *Seseli* L. species showed that the plants contain especially coumarins, cinnamic acid derivatives, sesquiterpene lactones, phenylpropanoid type compounds, and essential oils. Several biological activities focused particularly on the essential oils of *Seseli* species, including fungitoxic, insect-repellent, antimicrobial, anti-inflammatory, and analgesic activities [8, 9].

In our previous studies, coumarins were investigated on *Seseli* species [10, 11]. Moreover, the essential oils of *Seseli* species were analyzed in Turkey [12–16]. Recently, we investigated the antimicrobial, anti-inflammatory, and antinociceptive activities of Turkish *Seseli* species [17, 18].

Up to now, *S. hartvigii* has not been investigated regarding the chemical composition. In the present study, the *n*-hexane extract of aerial parts of *Seseli hartvigii* (AEF 21700, Herbarium of the Faculty of Pharmacy of Ankara University) were examined for coumarin type compounds that have various biological activities.

Air-dried and powdered aerial parts (1 kg) of *S. hartvigii* were consecutively extracted with *n*-hexane, EtOAc, and finally with MeOH under reflux for 8 h each. The *n*-hexane extract (47 g) was evaporated in vacuum to dryness and subjected to silica gel column chromatography eluting with a gradient system from *n*-hexane to EtOAc. Three known compounds – an angular pyranocoumarin [*cis*-(3′*R*,4′*R*)-3′-angeloyloxy-4′-acetyloxy-3′,4′-dihydroseselin] (isopteryxin) (**1**) and two simple coumarins, 6-(3′-methylbutenyl)-7-methoxycoumarin (suberosin) (**2**) and 5,7-dimethoxy-8-(3′-methyl-2′,3′-dihydroxybutenyl)-coumarin (mexoticin) (**3**), were isolated from this plant.

These compounds were identified by their physical (mp, $[\alpha]_D$) and spectroscopic specifications (^{1}H NMR, ^{13}C NMR, MS) and by comparison with literature data. The obtained spectra of the isolated compounds were in agreement with the appropriate literature data.

Isopteryxin (**1**) [*cis*-(3′*R*, 4′*R*)-3′-angeloyloxy-4′-acetyloxy-3′,4′-dihydroseselin]. Colorless cubic and glass-like crystal, mp 135–136°C, $[\alpha]_D^{20}$ –34.4° (*c* 1.0, $CHCl_3$), EIMS: $C_{21}H_{22}O7$ M^+, *m/z*, $I_{rel.}$, %), 386 (20.3), 286 (15.5), 245 (16.0), 244 (46.0), 229 (100.0, base peak), 191 (17.9), 190 (13.3), 83 (63.9), 55 (25.0); ^{1}H NMR (300 MHz, $CDCl_3$ δ, ppm, J/Hz): 6.23 (d, J= 9.5, H-3), 7.60 (d, J= 9.5, H-4), 7.35 (d, J= 8.4, H-5), 6.80 (d, J= 8.4, H-6), 5.40 (d, J= 5.1, H-3′), 6.59 (d, J= 5.1, H-4′), 2′ *gem*-Me 1.42, 1.43 (s), ester part 1.86 (t, J= 1.5, H-5″, COCC$\underline{H}_3$), 1.95 (dq, J = 7.3, J = 1.5, H-4″, CHC$\underline{H}_3$), 6.13 (qd, J= 7.3, J = 1.5, H-3″, C$\underline{H}$CH$_3$), 2.10 (OCOC$\underline{H}_3$, s).

Suberosin (**2**) [6-(3′-methylbutenyl)-7-methoxycoumarin]. Crystal type substance, mp 84–85°C, EIMS: $C_{16}H_{14}O_3$ M^+, *m/z*, $I_{rel.}$, %), 244 (72.0), 230 (15.0), 229 (100.0, base peak), 189 (13.6). ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm, J/Hz): 6.23 (d, J = 9.5, H-3), 7.62 (d, J= 9.5, H-4), 7.17 (s, H-5), 3.89 (s, 7-OC$\underline{H}_3$), 6.77 (s, H-8), 3.30 (d, J = 7.3, H-1′), 5.27 (t, J = 7.3, H-2′), 1.70 (s , H-4′) and 1.77 (s, H-5′).

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Mexoticin (3) [5,7-dimethoxy-8-(3′-methyl-2′,3′-dihydroxybutenyl)-coumarin]. Amorphous substance, $[\alpha]_D^{20}$+36.9° (*c* 1.0, $CHCl_3$), mp 180–183°C, EIMS: $C_{16}H_{20}O_6$ M^+, *m/z*, $I_{rel.}$, %), 308 (3.1), 250 (21.4), 249 (23.7), 220 (35.3), 219 (91.2), 207 (100, base peak), 161 (19.3). ^{1}H NMR (300 MHz, in $CDCl_3$, δ, ppm, J/Hz): 6.13 (d, J = 9.5, H-3), 7.98 (H-4, d, J = 9.5), 3.93 (s, 5-$OCH_3$and 7-OCH_3), 6.34 (s, H-6), 2.85 (dd, J = 9.9, J = 14.0, H-1′), 3.00 (dd, J = 2.7, J = 14.0, H-1′), 3.59 (dd, J =2.7, J = 9.9, H-2′), 1.30 (s, H-4′), 1.32 (s, H-5′).

Seseli hartvigii was investigated in the present study for the first time. To the best of our knowledge, this is the first report on the isolation of isopteryxin (**1**), suberosin (**2**), and mexoticin (**3**) from the plant.

The chemical constituents of this species seem to be typical of the genus *Seseli* and common for the Umbelliferae and Rutaceae family. In our future research, isolation of coumarin type compounds will be performed in polar fractions as well as in *n*-hexane extracts of *Seseli hartvigii*.

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