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RESEARCH ARTICLE

Chemical composition and antioxidant activity of *Sium sisarum* essential oils

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Abstract

The genus *Sium* (Apiaceae) is presented by perennials with fibrous roots, inflorescence paniculate-corymbose, white petals, minute sepals, slightly lateral compressed fruits in the Flora of Turkey. The essential oils of the fruits and aerial parts of *Sium sisarum* L. collected from two different localities Kavak and Ladik in Samsun, Turkey, were obtained by hydrodistillation. The essential oils were assigened as EO1 (fruit, Kavak), EO2 (aerial parts, Kavak), EO3 (fruit, Ladik), EO4 (aerial parts, Ladik). All samples were analyzed by gas chromatography (GC) and gas chromatography/mass spectrometry (GC/MS), simultaneously. *γ*-Terpinene (71.8, 64.2, 42.3, 39.0 %) and *p*-cymene (16.4, 23.4, 33.8, 33.0 %) were found as major constituents of the analysed samples, respectively. *β*-Pinene (7.7 %) and limonene (8.3 %) were identified as the major components for EO3. Also, *β*-pinene (4.0 %), limonene (10.0 %) and *ar*-curcumene (2.0 %) were found as the major components for EO4. Additionally, the quantitative *in vitro* testing using DPPH was conducted to determine the antioxidant capacity. UV absorbance of the samples were measured at 517 nm using a microplate spectrophotometer system. According to the assay results, antioxidant potential of the tested essential oils was comparatively weak (IC_{50} > 30 mg/mL).

Keywords: *Sium sisarum*, gas chromatography, gas chromatography-mass spectrometry, DPPH antioxidant activity

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Introduction

The genus *Sium* (Apiaceae) is describe as perennials with fibrous roots; petioles not persistent, leaves 1-pinnate with broad leaflets, inflorescence paniculate-corymbose, bracts and bracteoles present, sepals minute, petals white, fruit slightly compressed laterally; mericarps narrowly elliptic-oblong; dorsal and lateral ridges shortly elevated-spongiose; dorsal vittae three per vallecula, commissural six, in Flora of Turkey (Davis et al, 1972). *S. sisarum* is known as Skirret grows in Cyprus, Eastern Europe, Russia, Iran; Adana, Kars, Hakkari, Karabük and Samsun provinces in Turkey (Bakış et al., 2011). The roots of *S. sisarum* are very sweet and can be eaten raw or cooked. Skirret makes a great addition to soups, where its soft texture will cause it to break apart and act as a sweetener and thickener (Harvey, 1984).

Materials and Methods

Plant material

The *Sium sisarum* materials were collected in 2014 and 2015 from two different localities Kavak (A.Duran 10517 & M.Çelik) and Ladik (A.Duran 9987 & F.Altınordu) in Samsun province, Turkey. The fruits and aerial parts of *S. sisarum* were hydrodistillated for 3 h using Clevenger-type apparatus. The essential oils were coded as EO1 (fruit, Kavak), EO2 (aerial parts, Kavak), EO3 (fruit, Ladik), EO4 (aerial parts, Ladik). The essential oil yields were calculated as 2.0, 0.2, 1.3, and 0.2%, v/w, respectively.

Gas chromatography - flame ionization detection (GC-FID) analysis

The essential oils were analyzed by GC using a Hewlett Packard 6890 system (SEM Ltd, Istanbul, Turkey) and an HP Innowax fused silica capillary column (FSC) (60 m x 0.25 mm Ø, with 0.25 µm film thickness) was used with nitrogen at 1 mL/min. Initial oven temperature was 60 °C for 10 min, and increased at 4 °C/min to 220°C, then kept constant at 220 °C for 10 min and increased at 1 °C/min to 240 °C. Injector temperature was set at 250 °C. Percentage compositions of the individual components were obtained from electronic integration using flame ionization detection (FID, 250 °C) (Demirci, et al., 2008). Relative percentages of the separated compounds were calculated from FID chromatograms as cited in Table 1.

Gas chromatography - mass spectrometry (GC-MS) analysis

GC-MS analysis was performed with a Hewlett-Packard GCD, system (SEM Ltd, Istanbul, Turkey) and Innowax FSC column (60 m x 0.25 mm, 0.25 µm film thickness) was used with Helium. GC oven temperature conditions were as described above, split flow was adjusted at 50 mL/min, the injector temperature was at 250 °C. Mass spectra were recorded at 70 eV. Mass range was from m/z 35 to 425 as previously reported (Demirci, et al., 2008).

Identification of components

Identification of the essential oil components were carried out by comparison of their relative retentiontimes with those of authentic samples or by comparison of their relative retention index (RRI) to series of n-alkanes. Computer matching against commercial (Wiley GC-MS Library, MassFinder Software 4.0) (McLafferty & Stauffer, 1989, Hochmuth, 2008), and in-house "Başer Library of Essential Oil Constituents" built up by genuine compounds and components of known oils, as well as MS literature data (Joulain & König, 1998) was used for the identification as also previously reported in detail (Demirci, et al., 2008).

1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity

Serial dilutions were carried out with stock solutions (10 mg/mL) of the essential oils to obtain the concentrations of 10, 5, 25×10^{-1}, 125×10^{-2}, 625×10^{-3}, 3125×10^{-4} mg/mL. Diluted solutions were mixed with DPPH (Sigma Aldrich, USA) and allowed to stand for 30 min for any reaction to occur. The UV absorbance was recorded at 517 nm at room temperature using a microplate spectrophotometer. The experiment was performed three times and average absorption was noted for each concentration. Ascorbic acid was used as a positive control. The percentage of inhibition was calculated using equation. The IC50 value, which is the concentration of the test materials that inhibits 50% of the free radical concentration, was calculated as mg/mL (Kumarasamy et al., 2007).

$$\text{Percentage Inhibition} = \left[\frac{(\text{Abs}_{\text{control}} - \text{Abs}_{\text{sample}})}{\text{Abs}_{\text{control}}}\right] x100$$

Results and Discussion

The essential oils obtained by hydrodistillation from fruit and aerial parts of *S. sisarum* was analyzed by GC-FID and GC-MS. *γ*-terpinene (71.8, 64.2, 42.3, 39.0 %) and *p*-cymene (16.4, 23.4, 33.8, 33 %) were found as major constituents of all samples. *β*-pinene (7.7 %) and limonene (8.3 %) were identified as a major constituents for EO3. Also, *β*-pinene (4.0 %), limonene (10.0 %) and *ar*-curcumene (2.0 %) were found as a major constituents for EO4. Other constituents were given in Table 1.

1,1-Diphenyl-2-picrylhydrazyl (DPPH) radical scavenging activity was used to determine the antioxidant capacity of *S. sisarum*. However, IC_{50} values of essential oils were found more than 30 mg/mL. IC_{50} value of ascorbic acid which used as a positive control, was found 6.3 µg/mL. When the compared with ascorbic acid, the essential oils have shown weak DPPH radical scavenging activities.

To the best of our knowledge this is the first report on the phytochemical composition of *Sium sisarum* volatiles and its biological evaluation. Furhter bioassays are performed for further future insights.

Table 1. The Compositions of *Sium sisarum* Essential Oils

RRI[a]	Constituent	EO1 %[b]	EO2 %[b]	EO3 %[b]	EO4 %[b]
1032	*α*-Pinene	0.1	tr[c]	0.3	0.2
1035	*α*-Thujene	0.4	tr	0.3	0.2
1118	*β*-Pinene	1.3	1.1	7.7	4.0
1132	Sabinene	1.2	0.8	0.6	0.4
1174	Myrcene	0.7	0.3	0.5	0.3
1188	*α*-Terpinene	0.7	0.5	0.3	0.2
1203	Limonene	0.1	-	8.3	10.0
1218	*β*-Phellandrene	0.4	0.3	0.3	-
1255	*γ*-Terpinene	71.8	64.2	42.3	39.0
1280	*p*-Cymene	16.4	23.4	33.8	33.0
1296	Octanal	0.3	-	0.5	0.8
1298	Terpinolene	0.1	-	-	-
1452	*α*-*p*-Dimethyl styrene	-	-	-	0.2
1474	*trans*-Sabinene hydrate	0.1	-	-	-
1553	Linalool	-	-	0.3	0.4
1604	Thymol methyl ether	0.1	-	-	-
1611	Terpinene-4-ol	0.2	-	-	-
1614	Carvacrol methyl ether	0.1	-	tr	-
1655	(E)-2-Decenal	0.2	-	0.2	0.3
1700	Limonen-4-ol	-	-	-	0.3
1726	*α*-Zingiberen	1.0	1.7	0.3	0.5
1783	*β*-Sesquiphellandrene	1.1	2.0	0.4	1.2
1786	*ar*-Curcumene	0.8	1.7	0.9	2.0
1864	*p*-Cymen-8-ol	-	-	0.1	-
2030	Methyl eugenol	-	-	-	0.2
2084	Octanoic acid	-	-	tr	tr
2198	Thymol	0.1	-	tr	0.1
2214	*ar*-Turmerol	-	-	-	0.2
2239	Carvacrol	0.2	-	tr	0.4
2384	Dillapiol	tr	0.4	-	0.4
2670	Tetradecanoic acid	-	-	-	0.3
2700	Heptacosane	-	-	-	0.1
2900	Nonacosane	-	-	-	0.1
2931	Hexadecanoic acid	0.3	2.6	0.5	1.0
	Total	**97.7**	**99.0**	**97.6**	**95.8**

RRI [a]: Relative retention indices calculated against *n*-alkanes; b %: calculated from FID data. tr: Trace (< 0.1 %)

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