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Characterısatıon of volatıle compounds by spme and gc-fıd/ms of capers (*Capparis spinosa* L.)

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***Capparis spinosa* L. has highly biologically active natural substances. *C. spinosa* L. is rich in volatile components, and is becoming increasingly popular because of its components' potential role in contributing to human health. In this study, *s*olid phase microextraction (SPME) was used to analyze the volatile compounds identified in *C. spinosa* L. Seventeen compounds, constituting 93.5% of the oil composition of *C. spinosa* L. were isolated and characterized using GC-FID/MS. The most abundant chemical classes identified were aldehydes (18.2%) and monoterpene hydrocarbons (4.4%). Common components of *C. spinosa* L. identified were benzyl alcohol, octanoic acid, benzoic acid, α-terpinolene, carvacrol, zingerone and 4-fluoro benzaldehyde.**

Key words: *Capparis spinosa* L., essential oil, solid-phase microextraction/gas chromatography-mass spectrometry (SPME-GC-MS).

INTRODUCTION

Capparis spinosa L. (Capparaceae) is a widespread perennial shrub found both wild and cultivated in Mediterranean regions. It is known to possess medicinal and aromatic properties. While the ancient habitat is thought to be arid parts of western or central Asia, the plant is naturally distributed right along the Mediterranean Sea basin coast. Its habitat extends from the Canary Islands and the Atlantic coast of Morocco to the Black Sea to the Crimea and Armenia, and from there to the Caspian Sea and Iran in the east. Traditional Iranian medicine uses the fruits and root of *C. spinosa* to treat gout, as well as for their diuretic, astringent and tonic properties (Afsharypuor et al., 1998). Medicinal properties have also been ascribed to the flower buds, which are used to ameliorate hepatic functions or as a renal disinfectant. One study reported pronounced anti-inflammatory activity against carrageenan-induced edema in a rodent model (Al-Said et al., 1988).

C. spinosa L. is a popular aromatic in Mediterranean cuisine. The floral buds are familiarly known as capers. These are harvested in spring, prior to blossoming, and then kept in salt-water. They are used to add a spicy flavor to salads, pasta, meat, sauces and garnishes, and occupy an increasingly significant place in the food industry. The number of reports investigating caper flavor is minimal. Brevard et al. (1992) investigated the flavor profile of Moroccan capers, and Afsharypuor et al. (1998) that of capers from Iran. These two studies employed

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used distillation-based, volatile extraction techniques. Focus of late has been on developing sample preparationmethods without the use of solvents, while investigations of flavor in different foods is of increasing interest due to its association with food product quality.

The caper is believed to be rich in volatile organic compounds. The aim of this study was to determine semi quantitative differences in volatile organic compounds of *C. spinosa* L. by using SPME-GC-FID/MS analysis. Solid phase microextraction is an alternative technique for the extraction of organic volatiles from different sample, compared with traditional methods (Yaylı et al., 2014). Solid phase microextraction (Arthur and Pawliszyn, 1990) offers reliable analysis of highly complex mixtures of volatile organic compounds. This is the first detailed report on the volatile organic compound composition for the *C. spinosa* L. based on SPME and capillary GC-FID/MS analyses.

MATERIALS AND METHODS

Plant material

C. spinosa L. samples were purchased from herb markets in Gaziantep, Turkey, in June 2013.

Solid-phase microextraction

A manual SPME device including fiber was obtained from Supelco (USA). The fiber used to obtain volatile components was polydimethylsiloxane/divinyl-benzene (PDMS/DVB, 65 µm-blue hub plain).

The SPME fibers were conditioned for 5 min at 250°C in the GC injector. Conditioning time for subsequent assays was set at 4 min of desorption after each extraction. Extractions were performed at 50°C using an incubation time of 5 min and an extraction time of 10 min. Each sample was analyzed, and means were then calculated.

Gas chromatography-mass spectrometry (SPME-GC-MS)

To perform the SPME procedure, ~1.00 g of tree plant was placed in a 10 mL vial. The fiber coating was located on the head space for temperature and time (incubation and extraction times) values set on the basis of the experiment. Extractions took place with magnetic stirring. Fibers with extracted aroma compounds were subsequently injected into the GC injector (split mode). Thermal desorption then took place at 250°C for 4 min.

A Shimadzu 2010 Plus gas chromatograph coupled to a Shimadzu QP2010 Ultra mass selective detector was used for GC analysis. Separation took place with a Restek Rxi-5MS capillary column, 60 m length, 0.25 mm i.d. and 0.25 µm phase thickness. Split mode was employed. Initial oven temperature was 60°C for 2 min. This was then raised to 240°C at 3°C min^{-1}; 250°C was maintained for 4 min. Helium (99.999%) was employed as carrier gas at a constant flow-rate of 1 mL min^{-1}. Electronic impact mode (EI) was used for detection with the ionization voltage stabilized at 70 eV. Scan mode (40-450 *m/z*) was used for mass acquisition. Volatile compounds were identified by comparison of their RIs (relative to C7-C30 alkane standards), matching mass spectral data with those held in the FFNSC1.2 and W9N11 library of mass spectra and comparing the results with the literature (Bicchi et al., 2008; Mondello et al., 2008; Zellner et al., 2008).

RESULTS

SPME was used to obtain volatile organic compounds. These were subsequently analyzed with GC-FID/MS. Identification was made on the basis of comparison of GC Kovats retention indexes (RIs), with reference to a homologous series of *n*-alkanes, and of a comparison of mass spectral fragmentation patterns with data from the literature (Formisano et al., 2011). The chemical composition of the essential oils obtained from *C. spinosa* L. is presented in Table 1. The chemical class distributions of the volatile constituents are summarized in Table 2. Compounds were classified as terpenoids (monoterpene hydrocarbons, monoterpenoids), aldehydes, hydrocarbons and others (Table 2). The main components in the essential oils of *C. spinosa* L. are shown as benzyl alcohol, benzaldehyde, carvacrol, carvone, and terpinolene (Figure 1).

DISCUSSION

Aldehydes represented the main constituents of *Capparis spinosa* L., at 18.2%. The most common aldehydes were 4-fluoro benzaldehyde and benzaldehyde, at 12.9 and 3.5%, respectively. Romeo et al. (2007) reported that cinnamaldehyde (X = 396.63 ppm) and benzaldehyde (X = 311.34 ppm) were the most abundant aldehydes. Benzaldehyde is commonly found in volatile oils. This is explained by the presence, in parts of plants, of various glucosides which yield benzaldehyde, hydrocyanic acid and glucose at hydrolysis.

Benzyl alcohol, an aromatic alcohol and natural component of various plants, represented 39% of volatile constituents of *Capparis spinosa* L. Benzyl alcohol is normally oxidised rapidly to benzoic acid. Benzyl alcohol is conjugated with glycine in the liver and excreted as hippuric acid. Benzyl alcohol is used in a wide variety of cosmetic formulations as a scent component, and as a preservative in many injectable drugs and solvents, solvent and viscosity-lowering agent. Benzyl alcohol has been reported to establish time-, dose- and temperature-dependent hemolysis of erythrocytes in vitro. Critical hemolytic levels of benzyl alcohol to membranes have been calculated at approximately 500 nmoles/mg protein (approximately 54 microgram/mg protein) (Ohmiya and Nakai, 1978). Octanoic acid and benzoic acid represented the main components among the free acids in our study, constituting 18.2 and 6.6% of the identified chemical constituents, respectively. Most fatty acids naturally occur as esters or else are converted to alcohols, aldehydes, olefins, hydrocarbons and other secondary metabolites. Alcohols and aldehydes, the product of oxidative degradation of fatty acids, comprise the green leaf volatile complex of many plants. Alcohols a

Table 1. Isolation of volatile compouds from *Capparis spinosa* L. used SPME method with GC-FID-MS.

Compounds	%Area	Retention time	Retention İndex
4-Fluoro benzaldehyde	12.9	14.07	957
Benzaldehyde	3.5	14.39	982
β -Pinene	0.7	15.42	995
Octanal	0.8	15.92	1006
p-Cymene	0.2	17.15	1030
Benzyl alcohol	39.0	17.32	1038
α -Terpinolene	3.5	20.04	1101
Nonanal	0.8	20.22	1106
Benzene ethanol	1.8	20.79	1119
Benzoic acid	6.6	22.63	1161
Octanoic acid	18.2	22.94	1168
7-Hexadecenal	0.2	24.56	1206
Carvone	0.9	26.44	1251
Neryl acetate	0.4	26.65	1256
Carvacrol	1.8	28.64	1304
Tetradecane	1.0	32.42	1398
Zingerone	1.4	41.91	1656
Total	93.5		

Table 2. The chemical class distribution of the essential oil components of *C. spinosa* L.

Constituents	% Area	NC[a]
Monoterpene hydrocarbons	4.4	3
Monoterpenoids	2.7	2
Aldehyde	18.2	5
Hydrocarbones	1.0	1
Others	67.4	6
Total	93.7	17

[a]NC, Number of compound.

nd aldehydes, the product of oxidative degradation of fatty acids, comprise the green leaf volatile complex of many plants. The majority of fatty acids appear in the form of esters. They may also be converted into various alcohols, aldehydes, olefins, hydrocarbons and other secondary metabolites. Especially alcohols and aldehydes resulting from oxidative degradation of fatty acids constitute the green leaf volatile complex of a wide range of plants.

Terpenes constitute 4.4% of the aroma identified in *C. spinosa* L., the major representative being α-Terpinolene. Terpinolene is also used as a synthetic flavoring additive and scent enhancer. This means that humans are frequently exposed to it. Terpinolene is present in sage and rosemary, and has been reported to significantly lower the protein expression of AKT1 in K562 cells and to suppress cell proliferation (Okumura et al., 2012). Romeo et al. (2007) determined that terpenes constituted 5.8% of the aroma. That study also reported the presence of five sesquiterpenes (C-15) and 10 monoterpenes (C-10) in capers, the most important being the acyclic sesquiterpene trans-nerolidol, followed by the monoterpene 4-terpineol. In an earlier study, Brevard et al. (1992) described the monoterpene linalool and the sesquiterpene b-ionone as the only terpenes identified in capers from Morocco. The C-10 monoterpenes are frequently partly responsible for plant odor. The production of these monoterpenes frequently takes place in non-photosynthetic tissues in non-pigmented plastids known as the leucoplast during these cells' brief metabolic activity (Gershenzon and Croteau, 1990). Investigation of volatile terpenes has been highly significant in terms of resolving systematic problems. Several of these terpenes act as chemical

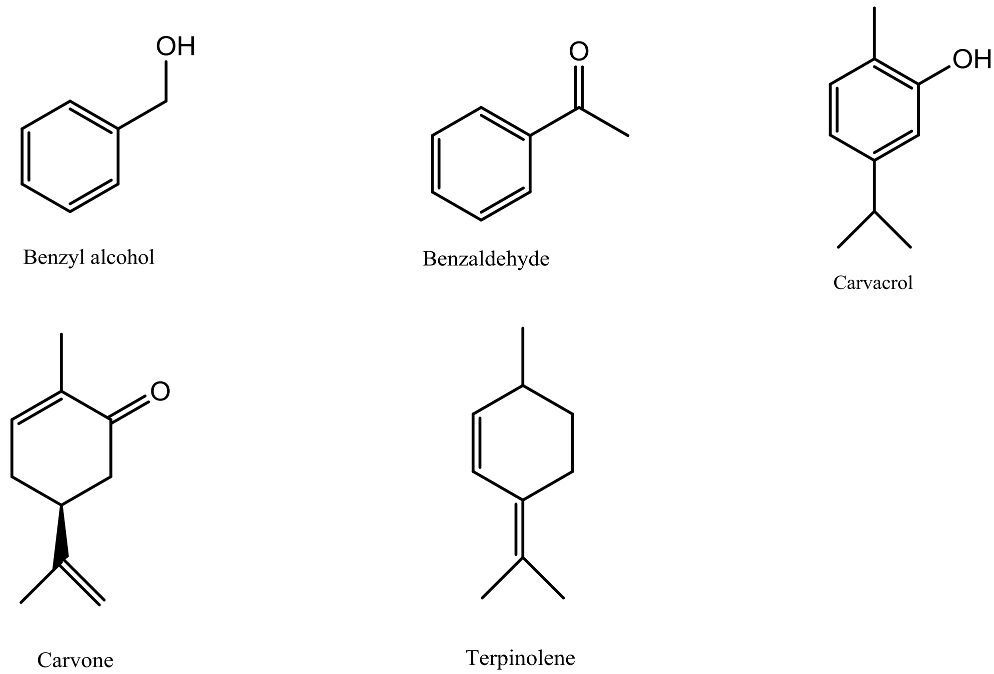

Figure 1. Main components in the essential oils of *Capparis spinosa* L.

communications for insects and other life forms. Their antimicrobial activity has also led to monoterpenes being used in the medicine and food industries (Beir and Nigg, 1992).

Carvacrol accounted for 1.8% of volatile constituents of *C. spinosa* L. Carvacrol is responsible for the biological activities of oregano, an important element in the food, spice and pharmaceutical industries. Carvacrol has been reported to exhibit antimicrobial, antitumor, antimutagenic, antigenotoxic, analgesic, antispasmodic, anti-inflammatory, angiogenic, antiparasitic, antiplatelet, antielastase, insecticidal, antihepatotoxic and hepatoprotective activities. It has also been demonstrated to be capable of use as a feed additive, in apiary and in the treatment of gastrointestinal disorders (Baser, 2008).

Zingerone constituted 1.4% of the volatile constituents of *C. spinosa* L. The free radical scavenging and antioxidant properties of the essential oils zingerone and eugenol, extracted from ginger and cloves, are well known (Kabuto and Yamanushi, 2011). Zingerone is currently used to treat a range of medical disorders. It reacts with free radicals responsible for injury and inflammation. As an antioxidant, it is also involved in lipid oxidation. In the presence of iron (III) and ascorbate, zingerone has a weak inhibitory effect on the oxidation of phospholipid liposomes to prevent heart-attacks. Zingerone has thus become a highly significant molecule, manufactured and synthesized for use in the pharmaceutical industry. Environmental factors, geographical locations and the parts of the plant used all have a powerful effect on essential oil chemical composition.

Conclusion

In our results, we generally observed aldehyde compounds with different ratios. A comparison with literature data on the chemical composition of volatile organic compound is difficult because of the great variability of the volatile compositions. The presence of volatile components depends on several parameters such as locality, the climatic conditions, season, extraction technique and analytical methods (Flamini et al., 2003).

Conflict of Interest

The authors declare they have no conflict of interest.

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