Hindawi
Journal of Food Quality
Volume 2021, Article ID 6620776, 9 pages
https://doi.org/10.1155/2021/6620776

Research Article

Volatile Profile in Different Aerial Parts of Two Caper Cultivars (*Capparis spinosa* L.)

Mar Grimalt,[1] Lucía Sánchez-Rodríguez,[2] Francisca Hernández,[3] Pilar Legua,[3] Ángel A. Carbonell-Barrachina,[2] María S. Almansa,[1] and Asunción Amorós[1]

[1]*Department of Applied Biology. Escuela Politécnica Superior de Orihuela, Miguel Hernández University, Ctra. Beniel, km 3.2, 03312, Orihuela, Alicante, Spain*
[2]*Department of Agro-Food Technology, Research Group Food Quality and Safety. Escuela Politécnica Superior de Orihuela, Miguel Hernández University, Ctra. Beniel, km 3.2, 03312, Orihuela, Alicante, Spain*
[3]*Department of Plant Science and Microbiology. Escuela Politécnica Superior de Orihuela, Miguel Hernández University, Ctra. Beniel, km 3.2, 03312, Orihuela, Alicante, Spain*

Correspondence should be addressed to Asunción Amorós; aamoros@umh.es

Received 13 November 2020; Revised 18 January 2021; Accepted 21 January 2021; Published 2 February 2021

Academic Editor: Alejandro Hernández

This research presents, for the first time, full volatile profiles of four aerial parts of caper plants (*Capparis spinosa* L.) from southeastern Spain. Volatile compounds in caper leaves and stems (together), flowers, flower buds, and fruits from two cultivars were identified and quantified using headspace-solid phase microextraction (HS-SPME) and gas chromatography with a mass spectrometry detector (GC-MS). Forty-three volatile compounds were identified in the caper shoots, 32 in caper flowers, with only 18, 10, and 6 compounds being found in flower buds, leaves, and fruits, respectively. The predominant compound in all studied materials was methyl isothiocyanate, with nerolidol, trans-2-hexenal, and nonanal playing key roles in flowers, leaves, and flowers buds, respectively. The two studied cultivars had the same volatile compounds but at very different concentrations, although the two studied cultivars are cultivated under the same climatic and agronomic conditions. Additionally, the predominant compounds, especially methyl isothiocyanate (6882 $mg \cdot kg^{-1}$ fw in flower buds of ORI 3 cultivar), can be separated and concentrated for future applications in food technology.

1. Introduction

Capparis spinosa L. (Capparaceae) has its origin in the regions of Central or Western Asia, but now, it is distributed in Southern Europe, North and East Africa, Madagascar, Southwest and Central Asia, Philippines, Indonesia, Papua New Guinea, Australia, and Oceania [1]. The species of the genus *Capparis* have been widely studied and used for edible or medicinal purposes, for its content in bioactive compounds and its numerous beneficial effects on antisclerosis, antihypertensive, anti-inflammatory, analgesic, antiasthmatic, antihyperlipidemic, hepatoprotective, antibacterial, and antifungal agents and diuretics, astringents, and tonics properties [2]. The infusion of stems and root crust were used as antidiarrheal and febrifuge remedies; fresh fruits were used for sciatica and dropsy; the combination of dried fruit and powder with honey was used to treat colds, gout, sciatica, and back pain, and it was also applied in the body for the treatment of epilepsy. Besides, the seeds were used to treat female sterility and to alleviate toothache [3]. Currently, the flower buds are marketed together with the caper fruit and the tenderest stems (the last 10 cm); before their commercialization, they are conserved in brine and are used as condiments and ingredients in salads and snacks.

There are works describing the main physicochemical characteristics of the caper fruits at 3 phenological states [4] and of the flower buds at 6 stages of development [5] and the phenological profile in Spanish cultivars [6]. Besides, there are few previous studies describing the volatile profiles *Capparis spinosa* L. cultivars. Cultivars from Morocco, Iran, and the Eolian Archipelago have been studied by Brevard et al. [7], Afsharypuor et al. [8], Romeo et al. [9], and Condurso et al. [10], respectively. The first two works used distillation-based and volatile extraction techniques. The volatile compounds generally show a great variability, which depends on climatological conditions, cultivar, maturity, and storage conditions among other factors [11].

According to our knowledge, this is the first work studying the chemical volatile profile of capers grown in Spain (Orihuela, Alicante), and it is intended to evaluate the different aerial parts: stems and leaves, flowers, flower buds, and caper fruit. The main innovative aspect of this study is that capper flowers are evaluated for the first time. They are edible, have a large size with white petals, delicate violet stamens, and specific aroma. These flowers can be introduced in modern dishes to make them more visual attractive, but their aroma and flavor must be also attractive to consumers and specially not having off-flavors. The rest of the aerial capper parts are also edible and have specific aroma and flavor. Thus, it is interesting to know the volatile composition of all cappers parts to be able to fully understand their potential role in modern cuisine, among other applications. For that purpose, headspace solid phase microextraction (HS-SPME) was used to isolate the volatile compounds, while the gas chromatography with a mass spectrometry detector (GC-MS) and FID detector (GC-FID) were used to identify and quantify these compounds, respectively. These analyses were conducted in the aerial parts of caper plants of two cultivars grown on the same plot. The information generated will help us understand the cultivar differences that may exist in the composition of volatile compounds in two cultivars grown under the same agronomic conditions.

2. Materials and Methods

2.1. Plant Material and Sample Processing. This research has been carried out in the different aerial parts of two caper cultivars, "Orihuela 3" ("ORI3") and "Orihuela 7" ("ORI7"). This caper cultivars were collected at the experimental field station of Miguel Hernandez University located in Orihuela (Alicante, Spain, 02°03′50″E, 38°03′50″N, and 25 masl). According to the agroclimatic classification of Papadakis [12], the experimental plot has a subtropical Mediterranean climate. The annual mean temperature is 19°C, with mild winters (11°C in January) and hot summers (28°C in August). A mean annual precipitation of 300 mm was recorded for the year of study, mostly falling in spring and autumn. The soil was a clay loam Xerofluvent [13], which showed high active calcium carbonate and low organic matter content, electrical conductivity, available phosphorus, and potassium exchange levels (Table 1). The irrigation water had a Cl^- concentration of 71–84 mg L^{-1} and an electrical conductivity of between 1.4 and 1.6 dS m^{-1}. The irrigation was with a dropper, watering 3 h per day, 5 days a week in the months of June–September, but in the months of October–December, watering was carried out 2 h per day, 3 days a week. A background fertilizer was made in autumn with 400 kg·ha^{-1} of 18% calcium superphosphate, 150 kg·ha^{-1} of 50% KCl, and 100 kg·ha^{-1} of 21% $(NH_4)_2SO_4$. A pruning was carried out in late autumn, leaving only the live vine as recommended by Melgarejo [14].

The plant material selection was manually carried out in July 2017. The different aerial parts collected during the process were classified into stems and leaves (together), flowers, flower buds, and caper fruits. Three different batches of samples were prepared using 10 uniform sampling units (stems and leaves, flower, flower buds, or fruits) of each cultivar; sampling units were manually picked at the same ripening stage and immediately were transported to the laboratory for preparation and further analyses. In this way, 30 sampling units per cultivar were used for the analyses. Once in the laboratory, the samples were washed with tap water for 2 min, frozen using liquid nitrogen, grinded for 10 s in a grinder (Taurus Aromatic Ver II; Taurus Group, Barcelona, Spain), and stored at −80°C until analyses were conducted. Once the collection period was over, the relevant analyses were carried out according to the aerial part to be determined.

2.2. Extraction Procedure of Volatile Aroma Compounds. The extraction of the volatile fraction was conducted using HS-SPME, and the analysis was carried out following the protocol developed by Cano-Lamadrid et al. [15]. Briefly, 5 g of the grinded sample was weighed, introduced in a 50 mL vial, and mixed with 15 mL of ultrapure water, 1.5 g of NaCl, and 15 μg of internal standard (β-ionone 15 mg kg^{-1}). The vial was placed in a bath at 36°C (to simulate the mouth temperature and establishing proper conditions to study the orthonasal olfaction), and after equilibration (15 min), a 50/30 μm divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) 2 cm fiber was exposed to the headspace during 30 min. Later, desorption of the volatile compounds from the fiber coating was performed in the injection port of the GC-MS during 3 min at 230°C. Extraction experiments were run in triplicate.

2.3. Chromatographic Analyses. First, the separation and identification of the volatile compounds was performed using a Shimadzu GC-17A gas chromatograph coupled with a Shimadzu QP-5050A mass spectrometer detector (Shimadzu Corporation, Kyoto, Japan). The GC-MS system was equipped with a TRACSIL Meta.X5, column (30 m × 0.25 mm × 0.25 μm film thickness; Teknokroma S. Coop. C. Ltd., Barcelona, Spain). Analyses were carried using He as carrier gas at a column flow rate of 0.6 mL·min^{-1} and a total flow of 13 mL·min^{-1} in a split ratio of 2 : 1. The oven program was the next: (i) 50°C for 0 min; (ii) increase of 3°C min^{-1} from 50°C to 170°C and hold for 1 min; and (iii) increase of 25°C·min^{-1} from 170°C to 300°C and hold for 1.8 min. The temperatures of the injector and detector were 230°C and 300°C, respectively. Samples were run using the scan mode in the range 40–350 m/z.

Identification was performed using 3 methods: (i) retention indices of each compound, (ii) GC-MS retention times (authentic standard), and (iii) mass spectra (Wiley 09

Table 1: Soil characteristics of the experimental plot.

Parameters*	
pH	8.37
Electrical conductivity ($dS{\cdot}m^{-1}$)	0.46
Sand (%)	26.2
Loam (%)	37.2
Clay (%)	36.6
Active $CaCO_3$ (%)	13.6
Oxidisable organic C ($g{\cdot}kg^{-1}$)	9.67
Total Kjeldahl N ($g{\cdot}kg^{-1}$)	1.44
Available P ($mg{\cdot}kg^{-1}$)	64
Exchangeable K ($g{\cdot}kg^{-1}$)	0.44
Exchangeable Ca ($g{\cdot}kg^{-1}$)	3.67
Exchangeable Mg ($g{\cdot}kg^{-1}$)	0.65

*Values on a dry matter basis.

MS library (Wiley, New York, NY, USA) and NIST14 (Gaithersburg, MD, USA)).

Finally, the quantification ($mg{\cdot}kg^{-1}$ fresh weight, fw) of the volatile compounds was performed on a gas chromatograph, Shimadzu 2010, with a flame ionization detector, FID. The column and chromatographic conditions were those previously reported for the GC-MS analysis. The injector temperature was 200°C, and N_2 was used as carrier gas (1 $mL{\cdot}min^{-1}$). β-Ionone was used as internal standard, and the areas from all compounds were normalized using its area; this compound was chosen after checking that it was not present in the volatile profiles of the samples under study. This analysis was run in triplicate.

2.4. Statistical Analysis. One-way analysis of variance (ANOVA) and Tukey's multiple range test were performed to compare experimental data and to determine significant differences among cultivars ($p < 0.05$). Principal component analysis (PCA) using Pearson correlation was also carried out. The software XLSTAT Premium 2016 (Addinsoft, New York, USA) and Statgraphics Plus (Version 3.1, Statistical Graphics Corp., Rockville, MA, USA) were used.

3. Results and Discussion

In the present research, 43 different volatile compounds have been identified in the four parts (flowers, leaves, flower buds, and caper fruits) of the caper plant under analysis (Tables 2–5). Results indicated that the predominant volatile component in all aerial parts of the caper was methyl isothiocyanate (chemical family: isocyanate). This compound is responsible for the pungent scent of the caper plant. In the flowers, leaves, stems, and flower buds, there were significant differences in the methyl isothiocyanate content between the cultivars "ORI3" and "ORI7" (710 and 2184 $mg{\cdot}kg^{-1}$ fresh weight (fw), 2654 and 1277 $mg{\cdot}kg^{-1}$ fw, and 6882 and 667 $mg{\cdot}kg^{-1}$ fw, respectively). In the study on the volatile composition of *Capparis spinosa* L. by Afsharypuor et al. [8] using leaves, fruits, and roots, the predominant compound was also methyl isothiocyanate, which agreed with current results. Sulfur compounds showed the highest amount in these cultivars, with methyl isothiocyanate being the main component. Isothiocyanates are derived from glucosinolates by enzymatic hydrolysis and are mainly found in Brassicaceae, although they are also identified in other families, such as Capparaceae and Caricaceae [10]. The glucosinolates are part of plant antiherbivore defenses, and methyl isothiocyanate can be considered as the most representative compound of the aromatic fraction of capers and derives from the degradation of glucocapparin [17].

Another compound having a high content was nonanal; in general, aldehydes provide oily and green flavor notes to plant matrices. Nonanal is one of the volatile compounds responsible for the characteristic "fresh green aroma" of fruits and vegetables. They are normally synthesized in the green organs of plants in response to wounds, and it is also the characteristic aroma of fruits and vegetables. The nonanal compound obtained from aldehydes C6 and C9 that have been derived from hydroperoxide lyase convert both types of hydroperoxide fatty acid derivatives into aldehydes that are often reduced in alcohols by alcohol dehydrogenases [17]. These C6/C9 aldehydes and alcohols have their origin in the biosynthesis of fatty acids, which is based on a pastidic set of acetyl-CoA generated from pyruvate, the final product of glycolysis [18]. The trends for nonanal were different according to the cultivar; "ORI7" has more contents than "ORI3" in flowers and caper fruits (3.5 and 1.7 $mg{\cdot}kg^{-1}$ fw and 29.2 and 1.32 $mg{\cdot}kg^{-1}$ fw, respectively), and in the case of leaves and flower buds, "ORI3" presented higher contents than "ORI7" (4.63 and 2.05 $mg{\cdot}kg^{-1}$ fw and 772.5 and 2.57, respectively). However, it is important to highlight that factors such as soil type, climatic conditions, stage of growth, and other factors can influence the volatile composition of plants, and specific analysis must be run to confirm results showed in this study.

Alcohols and aldehydes, derived from the oxidative degradation of fatty acids, form the volatile complex of most of the green leaf plants as cited by Romeo et al. [9]. According to the bibliography consulted, there are only few studies evaluating the volatile composition of the aerial parts of the caper plant (flowers, leaves, flower buds, and caper fruits). Regarding the flowers, there are not many previous studies of complete flowers. There are studies such as those carried out by Ascrizzi et al. [19], which determine the content of volatile compounds of the different parts of the flower, such as sepals, petals, and stamens, as well as complete flowers, leaves, and floral buttons. The results have been expressed in percentage; therefore, they are not fully comparable to the results showed in the present research. In any case, these authors reported that the predominant compound in flowers was methyl benzoate, as compared to methyl isothiocyanate (26882 $mg{\cdot}kg^{-1}$ fw in "ORI3" of flower buds). This may be due to the factors such as cultivar, farming practices, soil type, and method of volatiles isolation [20, 21].

Table 2: Volatile compounds of *Capparis spinosa* L. in flowers detected using headspace solid phase microextraction (HS-SPME) with GC-MS.

		RT	RI		Chemical family	ANOVA	ORI 3 ($mg{\cdot}kg^{-1}$)	ORI 7 ($mg{\cdot}kg^{-1}$)	Descriptors *
			Exp.	Lit.					
Flowers									
1	Methyl isothiocyanate	2.917	747	742	Isocyanates	**	709.80 b	2183.99 a	Pungent
2	3-Hexanol	3.752	827	811	Alcohol	**	34.70 b	96.64 a	Alcohol; medicinal
3	1-Hexanol	3.85	836	854	Alcohol	NS	19.76	20.76	Green; woody
4	Butyl isothiocyanate	4.989	924	943	Isocyanates	NS	4.54	6.38	—
5	Isobutyl isothiocyanate	5.42	947	na	Isocyanates	NS	3.53	5.19	—
6	Butyl 2-propenoate	5.502	951	na	Ester	**	0.17 b	1.06 a	—
7	1-Octen-3-ol	5.876	973	978	Alcohol	NS	0.64	0.95	Herbaceous; earthy; mushroom; green
8	6-Methyl-5-hepten-2-one	6.002	979	985	Ketone	**	1.66 b	4.30 a	Green; oily
9	Decane	6.266	998	1000	Hydrocarbon	**	2.16 a	0.03 b	—
10	2-Ethylhexanol	7.061	1024	1025	Alcohol	**	0.53 b	1.17 a	—
11	Limonene	7.273	1032	1033	Terpene	**	3.66 a	2.45 b	Lemon; orange; sweet
12	Benzeneacetaldehyde	7.659	1046	1045	Aldehyde	**	8.57 b	44.26 a	—
13	3,5-Octadien-2-one	9.059	1098	1098	Ketone	**	0.68 a	0.14 b	—
14	Undecane	9.133	1102	1100	Hydrocarbon	**	25.701 a	0.01 b	Faint
15	Methyl benzoate	9.213	1104	1102	Ester	**	0.04 b	103.27 a	Fruity
16	Nonanal	9.381	1106	1104	Aldehyde	**	1.74 b	3.50 a	Green; lemon; lime; meaty; oily; rose
17	Methyl octanoate	9.943	1122	1120	Ester	**	0.56 b	1.24 a	Green; citrus; fruity
18	Benzyl cyanide	10.642	1142	1148	Aldehyde	**	0.87 b	12.58 a	—
19	Octanoic acid	11.375	1162	1169	Acid	**	1.74 a	0.77 b	Cheese; oily
20	Decanal	13.102	1209	1203	Aldehyde	**	1.63 a	0.22 b	Floral; citrus; sweet
21	Linalyl acetate	15.058	1254	1257	Ester	NS	1.22	0.05	fruity; floral; sweet; pear
22	Nonanoic acid	15.417	1267	1273	Acid	**	1.36 a	0.05 b	Cheesy; waxy; tallow
23	Benzyl isocyanide	15.733	1275	na	Isocyanate	**	1.02 b	4.91 a	—
24	Benzyl isothiocyanate	19.767	1370	1361	Isocyanate	**	16.89 b	98.10 a	Cabbage
25	3-Methylindole	20.76	1393	1396	Indol	**	26.99 a	6.31 b	Fatty
26	Isoamyl benzoate	22.913	1445	1462	Ester	NS	17.94	8.97	Sweet
27	Neryl acetone	23.23	1452	1457	Ketone	NS	0.36	0.78	Sweet, fruity and floral
28	β-Farnesene	23.453	1457	1457	Terpene	**	5.46 b	26.60 a	Apple; orange; grapefruit juice; lime; pear
29	α-Farnesene (isomer 1)	25.033	1495	1504	Terpene	**	20.29 a	0.43 b	Apple; orange; grapefruit juice; lime; pear
30	α-Farnesene (isomer 2)	25.609	1509		Terpene	**	1.75 a	0.64 b	Apple; orange; grapefruit juice; lime; pear
31	Methyl laureate	25.74	1528	1524	Ester	NS	0.18	0.89	—
32	Nerolidol	27.974		1713	Terpene	NS	143.75	193.73	Apple; green; citrus; woody; rose

RT, retention time; RI, retention indexes; Lit., literature (NIST 2011); Exp., experimental; NS, not significant at $p < 0.05$; ** significant at $p < 0.05$. Values (mean of 3 replications) in each row followed by the same letter were not significantly different ($p < 0.05$). *Descriptors reference [16].

Thirty-two volatile compounds were identified and quantified in flowers (Table 2); nerolidol was the predominant compound after methyl isothiocyanate. Significant differences between "ORI3" and "ORI7" cultivars were found with nerolidol content being 144 and 194 $mg{\cdot}kg^{-1}$ fw, respectively. The sensory descriptors of this compound are wood, green, apple, citrus, or rose and can be attractive for consumers. In the current study, an important terpene content was also found in flowers as limonene, β-farnesene, α-farnesene (isomers 1 and 2), and nerolidol, which have fruity aroma notes such as lemon, orange, sweet, lime, pear, or grapefruit. This can be due, among other facts, to terpenes acting as chemical messages for insects and other animals, which is essential to carry out pollination [9]. One of the important uses of the caper throughout the history has been its medicinal use, which is linked to its high terpene content and their high antimicrobial activity [22]. Regarding total terpene content in flower in this research, "ORI3" had 174.9 $mg{\cdot}kg^{-1}$ as compared to 223.8 $mg{\cdot}kg^{-1}$ of the cultivar "ORI7." It also found a high content in benzyl isothiocyanate (chemical family: isocyanate); although there were significant differences between both cultivars, the cultivar "ORI7"

Table 3: Volatile compounds of *Capparis spinosa* L. in leaves and stems detected using headspace solid phase microextraction (HS-SPME) with GC-MS.

		RT	RI		Chemical family	ANOVA	ORI 3 (mg·kg^{-1})	ORI 7 (mg·kg^{-1})	Descriptors*
			Exp.	Lit.					
Leaves									
1	Methyl isothiocyanate	2.90	739	742	Isocyanate	**	2653.52 a	1276.89 b	Pungent
2	trans-2-Hexenal	3.84	841	848	Aldehyde	**	307.46 a	160.80 b	Almond; apple; green; vegetable; plum; sweet
3	Butyl isothiocyanate	4.98	926	943	Isocyanate	NS	2.98	1.56	—
4	Isobutyl isothiocyanate	5.40	949	na	Isocyanate	**	22.83 a	6.52 b	—
5	1-Heptanol	5.64	951	970	Alcohol	NS	0.83	1.28	—
6	2,4-Heptadienal (isomer 1)	6.33	999	999	Aldehyde	NS	3.73	4.29	—
7	Octanal	6.40	1002	1001	Aldehyde	**	2.03 a	0.50 b	Fatty; honey; citrus; fruity
8	2,4-Heptadienal (isomer 2)	6.70	1013	1012	Aldehyde	NS	9.22	7.79	—
9	Nonanal	9.35	1106	1071	Aldehydes	NS	4.63	2.05	Apple; fatty; green; lemon; lime; oily; rose; nutty; waxy; meaty; melon; grape
10	Benzyl isocyanide	19.73	1369	1353	Isocyanate	**	43.09 a	14.91 b	—

RT, retention time; RI, retention indexes; Lit., literature (NIST 2011); Exp., experimental; NS, not significant at $p < 0.05$; ** significant at $p < 0.05$. Values (mean of 3 replications) in each row followed by the same letter were not significantly different ($p < 0.05$). *Descriptors reference [16].

Table 4: Volatile compounds of *Capparis spinosa* L. in flower buds detected using headspace solid phase microextraction (HS-SPME) with GC-MS.

		RT	RI		Chemical family	ANOVA	ORI 3 (mg kg^{-1})	ORI 7 (mg kg^{-1})	Descriptors*
			Exp.	Lit.					
Flower buds									
1	Ethyl p-hydroxybenzoate	2.407	1528	na	Isocyanate	**	99.12 a	0.11 b	—
2	Methyl isothiocyanate	2.836	736	747	Isocyanate	**	6881.76 a	667.34 b	Pungent
3	trans-2-Hexenal	3.778	839	848	Aldehyde	**	854.39 a	6.03 b	Almond; apple; green; vegetable; plum; sweet
4	2,4-Heptadienal (isomer 1)	6.295	999	999	Aldehyde	**	67.33 a	1.10 b	—
5	Octanal	6.392	1002	1001	Aldehyde	**	43.37 a	0.16 b	Fatty; honey; citrus; fruity
6	2,4-Heptadienal (isomer 2)	6.663	1012	1013	Aldehyde	NS	10.09	3.42	—
7	Limonene	7.208	1032	1033	Terpene	**	26.01 a	0.22 b	Lemon; orange; sweet
8	Benzeneacetaldehyde	7.606	1045	1045	Aldehyde	**	507.75 a	0.03 b	—
9	1-Octanol	8.223	1068	1070	Alcohol	**	22.27 a	0.99 b	Fatty; woody; citrus; waxy
10	3,5-Octadien-2-one	9	1095	1098	Ketone	**	49.19 a	0.45 b	—
11	Methyl benzoate	9.156	1101	1106	Isocyanate	**	650.18 a	2.80 b	Fruity
12	Nonanal	9.318	1105	1104	Aldehyde	**	772.46 a	2.57 b	Green; lemon; lime; meaty; oily; rose
13	Ethyl benzoate	11.433	1168	1153	Isocyanate	NS	0.90	1.12	Anise; banana; berry; cherry; grape; floral; minty; plum; vanilla
14	Octanoic acid	11.588	1163	1169	Acid	**	77.59 a	0.05 b	Cheese; oily
15	Decanal	13.05	1208	1203	Aldehyde	**	88.42 a	0.37 b	Floral; citrus; sweet
16	Nonanoic acid	15.363	1266	1273	Acid	**	205.99 a	0.33 b	Cheesy; waxy; tallow
17	Methyl 2-hydroxy-5-methylbenzoate	17.614	1319	na	Isocyanate	**	148.47 a	1.93 b	—
18	Decanoic acid	19.54	1364	1371	Acid	**	36.08 a	0.02 b	Fatty; citrus

RT, retention time; RI, retention indexes; Lit., literature (NIST 2011); Exp., experimental; NS, not significant at $p < 0.05$; **significant at $p < 0.05$. Values (mean of 3 replications) in each row followed by the same letter were not significantly different ($p < 0.05$). *Descriptors reference [16].

Table 5: Volatile compounds of *Capparis spinosa* L. in fruits detected using headspace solid phase microextraction (HS-SPME) with GC-MS.

		RT	RI		Chemical family	ANOVA	ORI 3 (mg·kg^{-1})	ORI 7 (mg·kg^{-1})	Descriptors *
			Exp.	Lit.					
Fruits									
1	Methyl isothiocyanate	2.93	733	747	Isocyanate	NS	1991.75	2352.37	Pungent
2	trans-2-Hexenal	3.84	836	848	Aldehyde	**	0.93 b	20.05 a	Almond; apple; green; vegetable; plum; sweet
3	2,4-Heptadienal (isomer 1)	6.32	999	1009	Aldehyde	NS	0.08	10.30	—
4	Limonene	7.13	999	1009	Terpene	**	0.39 b	13.31 a	Lemon; orange; sweet
5	4-Heptenal	8.52			Aldehyde	NS	0.56	8.92	Green; vegetable; fatty
6	Nonanal	9.33	1077	985	Aldehyde	**	1.32 b	29.19 a	Apple; fatty; green; lemon; lime; oily; rose; nutty; waxy; meaty; melon; grape

RT, retention time; RI, retention indexes; Lit., literature (NIST 2011); Exp., experimental; NS, not significant at $p < 0.05$; **significant at $p < 0.05$. Values (mean of 3 replications) in each row followed by the same letter were not significantly different ($p < 0.05$). *Descriptors reference [16].

presented a higher concentration (98.1 mg·kg^{-1} fw) compared to cultivar “ORI3” (16.9 mg·kg^{-1} fw). This compound gives a slight cabbage smell to caper flowers. In this research could be observed that the predominant chemical family present in flowers was isocyanates. Moreover, 3-hexanol (chemical family: alcohol) also showed high contents, with significant differences between cultivars, “ORI7” 96.6 mg·kg^{-1} fw and “ORI3” 34.7 mg·kg^{-1} fw. On the other hand, β-farnesene (chemical family: terpene) also had a high content, with again differences between cultivars: “ORI7” 26.6 mg·kg^{-1} fw and “ORI3” 5.46 mg·kg^{-1} fw.

A total of 10 volatile compounds had been identified in the caper leaves (Table 3). The compounds trans-2-hexenal (aldehyde) presented a high content (after methyl isothiocyanate), with 308 and 161 mg·kg^{-1} fw in “ORI3” and “ORI7,” respectively. This compound has an almond, apple, green, vegetable, plum, and sweet odor. It also showed an important content in benzyl isocyanide (chemical family: isocyanate), with “ORI3” having a higher content that “ORI7” (43.1 and 14.9 mg·kg^{-1} fw, respectively). There were no previous studies on the composition of volatiles in caper leaves. In the study made by El-Ghorab et al. [23] with *Capparis ovata* Desf. var. canescens cultivated in Turkey, it was reported that the most abundant compound in caper buds was benzyl alcohol (20.4%) and methyl isothiocyanate in leaves (20.0%). In the current experiment, new compounds have been reported probably due to different cultivars being studied, among other factors.

In flower buds, 18 volatile compounds (Table 4) had been identified, with trans-2-hexenal (aldehyde) predominating in the “ORI3” cultivar (854 mg·kg^{-1} fw), as compared to only 6.03 mg·kg^{-1} fw in “ORI7” samples, after methyl isothiocyanate in both cultivars. This aldehyde has an aroma resembling to vegetable, green, plum, apple, almond, green, and sweet. The second relevant compound in the caper flower buds was nonanal (aldehyde) with 772.46 and 2.57 mg·kg^{-1} fw in “ORI3” and “ORI7,” respectively. This compound has an aroma resembling to green, lemon, lime, meaty, oily, and rose. Then is methyl benzoate (isocyanate) with 650 and 2.80 mg·kg^{-1} fw in “ORI3” and “ORI7,” respectively. Also, benzeneacetaldehyde showed high contents, with high contents in the “ORI3” cultivar (508 mg·kg^{-1} fw) and only trace content in the cultivar “ORI7” (0.03 mg·kg^{-1} fw). The presence in food of aliphatic aldehydes, acids, and alcohols such as trans-2-hexenal, hexanal, nonanoic acid, and 1-octanol is related to fat oxidation reactions. These substances have been found in a variety of food products including meats and processed meats, fruits, as well as dairy and grain products. More specifically, they have been associated with green/grassy/vegetable aromatics in fruits and vegetables [10]. Caper flower buds have been previously studied; for instance, Romeo et al. [9] studied *Capparis spinosa* L. from the Eolian Archipelago. In general, contents reported in this previous study were lower than those found in the current experiment. For instance, in flower buds, methyl isothiocyanate had a content of 441 mg·kg^{-1} in the Eolian samples and 26882 mg·kg^{-1} in the Spanish ones; a similar trend was found for nonanal: 773 mg·kg^{-1} fw in “ORI3” and 11.32 ppm for the Eolian samples.

In fruits, only 6 volatile compounds were found (Table 5). Most of these compounds showed no significant differences between the two cultivars under study “ORI3” and “ORI7’, R except for the cases of trans-2-hexenal (20.05 and 0.93 mg·kg^{-1} fw in “ORI7” and “ORI3,” respectively), limonene (13.31 and 0.39 mg·kg^{-1} fw in “ORI7” and “ORI3, R respectively), and nonanal (29.2 and 1.3 mg·kg^{-1} fw in “Ori7” and “ORI3” respectively). Methyl isothiocyanate was identified as the predominant volatile compound, in the study by Afsharypuor et al. [8], found in fruits de caper plant.

Figure 1 shows the content of volatile compounds grouped by chemical family. In flowers, isocyanates followed

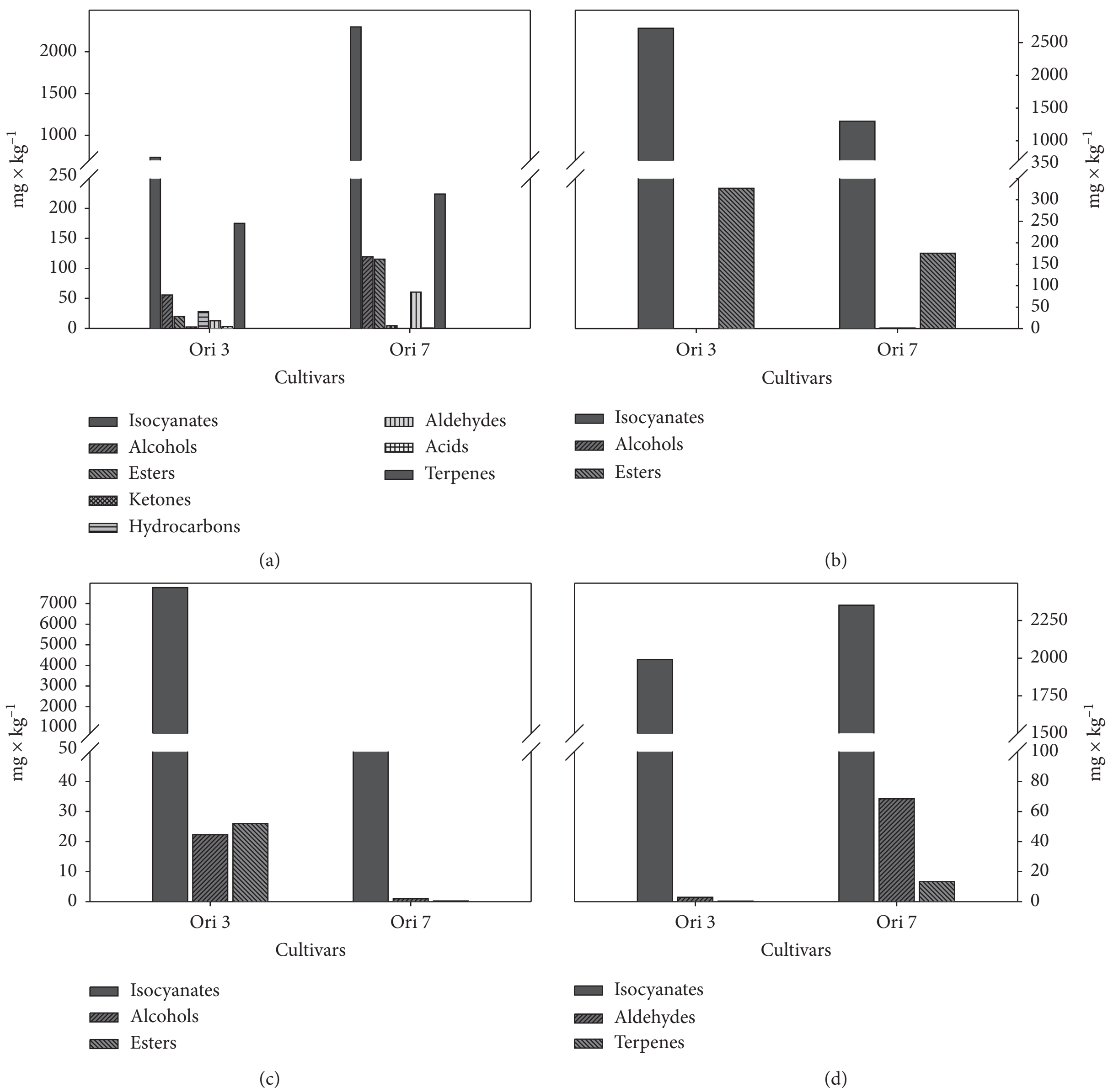

Figure 1: Identified families in both cultivars, "ORI3" and "ORI7," in the aerial parts of *Capparis spinosa* L. expressed in mg·kg^{-1} of fresh weight of flowers (a), leaf and stems (b), flower buds (c), and caper fruits (d).

by terpenes predominated in the volatile profiles of both cultivars (Figure 1(a)). Figure 1(b) represents the volatile profiles of caper leaves and shows more simple profiles, with isocyanates predominating over alcohols and esters. Figure 1(c) shows that the volatile contents in "ORI3" flower buds were much higher than those of the "ORI7" samples. Finally, capers fruits had significantly higher content of volatiles in "ORI7" as compared to "ORI3" samples (Figure 1(d)).

Figure 2 shows a principal component analysis (PCA) biplot (axes F1 and F2: 74.74%) where all the compounds and the different parts of caper and the two cultivars have been represented. The PCA is a very useful tool to show, in a graphic way, which compounds predominate in the different aerial parts of caper plants; 3 well-differentiated groups can be observed. In this way, in the upper left quadrant, the flowers of both cultivars were grouped, which had a very similar volatile composition. Flowers were associated with a high number of volatile compounds, including nerolidol and benzyl isothiocyanate; this high number of compounds is indicative of a complex aroma profile. Next, in the upper right quadrant, "ORI3" flower buds were positioned. The flower buds of "ORI7" showed a volatile profile similar to those of caper leaves and fruits of both cultivars "ORI3" and "ORI7." It is interesting to point out that methyl isothiocyanate was grouped close to "ORI3" flower buds, which are characterized by a more pungent flavor than that of the "ORI7" flower buds.

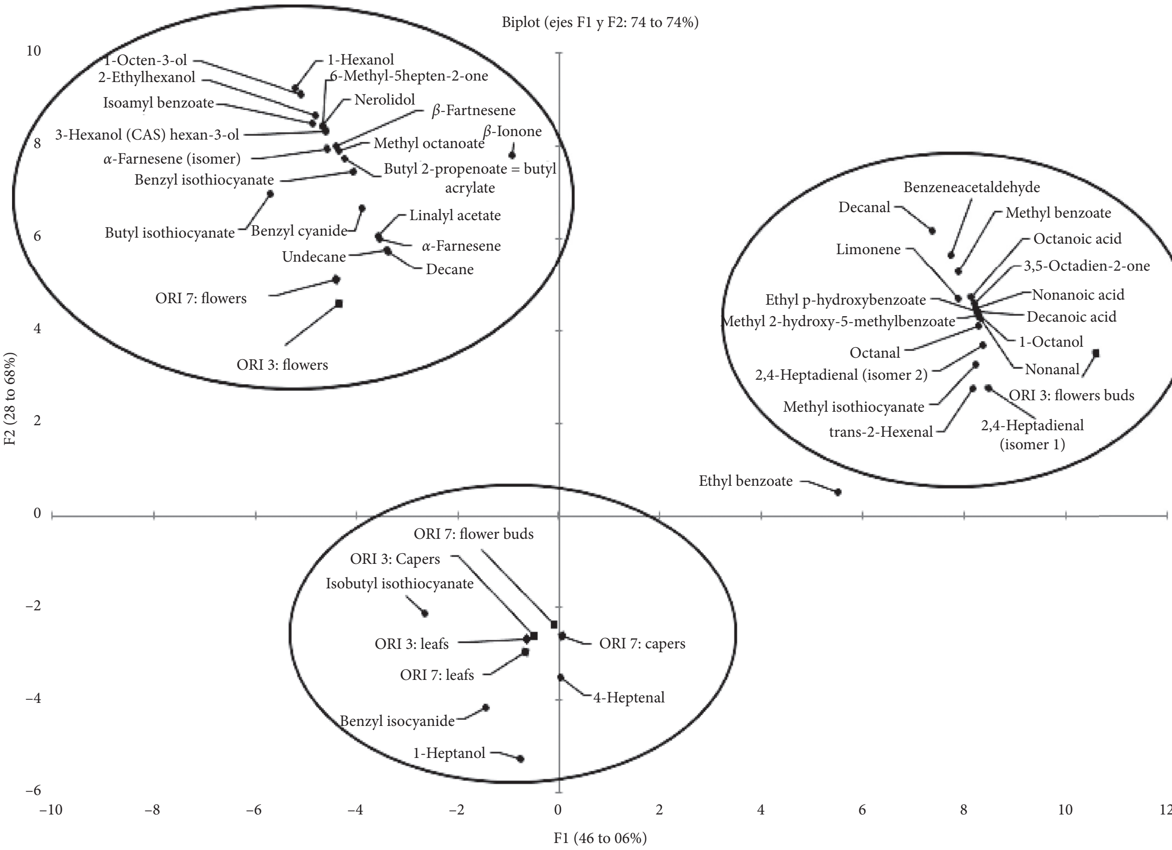

Figure 2: Principal component analysis (PCA) of different aerial parts of *Capparis spinosa* L. (●) and volatile compounds (◆).

4. Conclusions

Results showed that the two cultivars ("ORI3" and "ORI7") had the same volatile profile but compounds were present at very different concentrations, although plants were grown under the same climatic and agronomic conditions, indicating that they are cultivar-dependent. Caper flowers had the more complex profile, with 32 volatile compounds isolated, identified, and quantified: 5 isocyanates, 4 alcohols, 8 esters, 2 ketones, 2 hydrocarbons, 5 terpenes, 4 aldehydes, and 2 acids. Flower buds had a profile with 18 volatile compounds isolated, identified, and quantified: 5 isocyanates, 7 aldehydes, 1 terpene, 1 alcohol, 1 ketone, and 3 acids. Leaf capers had a profile with 10 volatile compounds: 4 isocyanates, 5 aldehydes, and 1 alcohol. Caper fruits had profiles with 6 volatile compounds, which do not have a strong aroma: 1 isocyanate, 4 aldehydes, and 1 terpene. The chemical family predominating the volatile profile of caper shoots was isocyanates, mainly due to the content of methyl isothiocyanate. In the caper flowers and fruits, the cultivar "ORI7" had higher contents of volatiles as compared to the "ORI3" samples. The opposite trend regarding cultivars was found in leaves and flower buds, with "ORI3" samples having the highest contents. The results demonstrated that volatiles profiles allowed distinguishing caper cultivars because they are cultivar-dependent and that capper flowers have a complex and rich volatile profile besides an attractive appearance that will make them very useful for modern cuisine purposes.

Data Availability

The original data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Acknowledgments

This research was funded by Consellería de Educación, Investigación, Cultura y Deportes de la Generalitat Valenciana from Spain (AICO-2016/015).

References

[1] S. Fici, "A taxonomic revision of the *Capparis spinosa* group (Capparaceae) from the Mediterranean to Central Asia," *Phytotaxa*, vol. 174, 2014.
[2] T. Gull, F. Anwar, B. Sultana, M. A. C. Alcayde, and W. Nouman, "Capparis species: a potential source of bioactives and high-value components: a review," *Industrial Crops and Products*, vol. 67, pp. 81–96, 2015.
[3] A. Al-Snafi, "The chemical constituents and pharmacological effects of *Capparis spinosa* an over view," *Indian Journal of Pharmaceutical Sciences*, vol. 5, pp. 93–100, 2015.
[4] M. Grimalt, F. Hernández, P. Legua, M. S. Almansa, and A. Amorós, "Physicochemical composition and antioxidant

activity of three Spanish caper (*Capparis spinosa* L.) fruit cultivars in three stages of development," *Scientia Horticulturae*, vol. 240, pp. 509–515, 2018.
[5] M. Grimalt, P. Legua, F. Hernández, A. Amorós, and M. S. Almansa, "Antioxidant activity and bioactive compounds contents in different stages of flower bud development from three Spanish Caper (*Capparis spinosa* L.) cultivars," *Horticultural Journal*, vol. 88, pp. 410–419, 2019.
[6] A. Wojdyło, P. Nowicka, M. Grimalt et al., "Hernández Polyphenol compounds and biological activity of caper (Capparis spinosa L.) flowers buds," *Plants*, vol. 8, p. 539, 2019.
[7] H. Brevard, M. Brambille, A. Chaintreau, and J. P. Marion, "Occurrence of elemental sulphur in capers (*Capparis spinosa* L.) and first investigation of the flavor profile," *Flavour and Fragrance Journal*, vol. 7, pp. 313–321, 1992.
[8] S. Afsharypuor, K. Jeiran, and A. Arefian, "First investigation of the flavour profiles of the leaf, ripe fruit and root of *Capparis spinosa* var. mucronifolia from Iran," *Pharmaceutica Acta Helvetiae*, vol. 72, pp. 307–309, 1998.
[9] V. Romeo, M. Ziino, D. Gruiffrida, C. Condurso, and A. Verzera, "Flavour profile of capers (*Capparis spinosa* L.) from the Eolian Archipelago by HS-SPME/GC-MS," *Food Chemistry*, vol. 101, pp. 1272–1278, 2007.
[10] C. Condurso, A. Mazzaglia, G. Tripodi et al., "Sensory analysis and head-space aroma volatiles for the characterization of capers from different geographic origin," *Journal of Essential Oil Research*, vol. 28, pp. 185–192, 2016.
[11] L. Andreu-Coll, L. Noguera-Artiaga, A. A. Carbonell-Barrachina, P. Legua, and F. Hernández, "Volatile composition of prickly pear fruit pulp from six Spanish cultivars," *Journal of Food Science*, vol. 85, pp. 358–363, 2020.
[12] Anonimus, *Atlas agroclimatico nacional de España, Tomo III*, MAPA, Madrid, Spain, 1986.
[13] Soil Survey Staff, *Keys to Soil Taxonomy*, USDA-NRCS, Washington, DC, USA, 10th edition, 2006.
[14] P. Melgarejo, *Tratado de Fruticultura para zonas áridas y semiáridas. Vol. I*, Mundi-Prensa, Madrid, Spain, 2000.
[15] M. Cano-Lamadrid, L. Lipan, F. Hernández et al., "Quality parameters, volatile composition, and sensory profiles of highly endangered Spanish citrus fruit," *Journal of Food Quality*, vol. 2018, Article ID 3475461, 13 pages, 2018.
[16] SAFC, *Sigma-Aldrich*, Flavors and Fragances Sigma-Aldrich, Madrid, Spain, 2014.
[17] C. Gigot, M. Ongena, M. L. Fauconnier, J. P. Watherlet, P. d Jardin, and P. Thonart, "The lipoxygenase metabolic pathway in plants: potential for industrial production of natural green leaf volatile," *Biotechnology, Agronomy, Society and Environment*, vol. 14, pp. 451–460, 2010.
[18] N. Duradeva, A. Klempien, J. K. Muhlemann, and I. Kaplan Biosynthesis, "Function and metabolic engineering of plant volatile organic compounds," *Tansley Review*, vol. 198, pp. 16–32, 2012.
[19] R. Ascrizzi, P. L. Cioni, G. Giusti, L. Pistelli, and G. Famini, "Patterns in volatile Emission of different aerial parts of caper (*Capparis spinosa* L.)," *Chemistry & Biodiversity*, vol. 13, pp. 904–912, 2016.
[20] T. Kulisic-Bilusic, I. Blazevic, B. Dejanovic, M. Milos, and G. Pifat, "Evaluation of the antioxidant activity of essential oils from caper (*Capparis spinosa*) and sea fennel (*Crithmum maritimum*) by different methods," *Journal of Food Biochemistry*, vol. 34, pp. 286–302, 2010.
[21] I. Blazevic and J. Mastelic, "Free and bound volatile of rocket (*Eruca sativa* Mill.)," *Flavour and Fragrance Journal*, vol. 23, pp. 278–285, 2008.
[22] R. C. Beir and H. N. Nigg, "Natural toxicant in foods," in *Phytochemical Resources for Medicinal and Agriculture*, H. N. Nigg and D. S. Seigler, Eds., pp. 247–367, Plenum Press, New York, NY, USA, 1992.
[23] A. El-Ghorab, T. Shibamoto, and M. Musa, "Chemical composition and antioxidant activities of buds and leaves of capers (*Capparis ovata* desf. var. canescens) cultivated in Turkey," *Journal of Essential Oil Research*, vol. 19, pp. 72–77, 2007.