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Elucidation of Analytical–Compositional Fingerprinting of Three Different Species of Chili Pepper by Using Headspace Solid-Phase Microextraction Coupled with Gas Chromatography–Mass Spectrometry Analysis, and Sensory Profile Evaluation

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Abstract: The aim of the present study was to determine the volatile compounds of three different species of chili peppers, using solid-phase microextraction (SPME) methods in combination with gas chromatography–mass spectrometry (GC-MS). The detection of marker aroma compounds could be used as a parameter to differentiate between species of chili peppers for their detection and traceability in chili pepper food. The sensorial contribution was also investigated to identify the predominant notes in each species and to evaluate how they can influence the overall aroma. Three different pepper species belonging to the *Capsicum genus* were analyzed: *Chinense*, *Annuum*, and *Baccatum*. A total of 269 volatile compounds were identified in these species of chili peppers. The *Capsicum annum* species were characterized by a high number of acids and ketones, while the *Capsicum chinense* and *Capsicum baccatum* were characterized by esters and aldehydes, respectively. The volatile profile of extra virgin olive oils (EVOOs) flavored with chili peppers was also investigated, and principal component analysis (PCA) and hierarchical cluster analysis (HCA) of the volatile profiles were demonstrated to be a powerful analytical strategy for building a model that highlights the potential of a volatile characterization approach for use in evaluating food traceability and authenticity.

Keywords: solid-phase microextraction (SPME); GC-MS; LRI; volatile fraction; chili peppers; food; marker; principal component analysis (PCA); hierarchical cluster analysis (HCA); EVOOs; sensory profile

1. Introduction

Chili peppers are used as food or spice and are widely used by the food industry as an ingredient for different kinds of flavored and spiced products. The *genus Capsicum* comprises five species: *Capsicum annuum* (containing NuMex, Jalapeno, and Bell varieties), *Capsicum frutescens* (containing the Tabasco variety), *Capsicum chinense* (containing the Habanero and Scotch Bonnet varieties), *Capsicum baccatum* (containing the Aji varieties), and *Capsicum pubescens* (containing the Rocoto and Manzano varieties) [1]. Even though the volatile profile of chili peppers *belonging* to the *Capsicum annuum* species has been analyzed, the volatile profile of *C. baccatum* has not been well investigated [2]. Furthermore, volatile compounds in *C. chinense* were identified and quantified as in previous articles [3–8], but

no direct comparison between the volatile profile of different *C. chinense* peppers and other pepper species has been made.

The aim of the present study was to analyze, by using solid-phase microextraction–gas chromatography (SPME-GC), the volatile profiles of 17 pepper varieties belonging to three of the five major cultivated species to assess the quality of the analyzed cultivars and to determine the marker compounds responsible for their aromatic characteristics and thus identify them as additives in food products.

Most of the studies presented in the literature were limited to the identification of volatiles without any sensorial tests, and therefore, the real contribution of individual compounds to the overall aroma has not been accurately established. In this respect, the sensory profile of chili peppers was also investigated in order to find a correlation with volatile components and to evaluate which notes contribute the most to the perceived aroma.

Furthermore, the volatile profile of chili-pepper-flavored foods has not been investigated in depth, and the results regarding the capsaicinoids content have mostly been investigated. For this reason, the volatile profile of three commercial extra virgin olive oils (EVOOs) flavored with chili pepper was examined by gas chromatographic analysis, comparing their profile with that of conventional unflavored extra virgin oils.

The linear retention index (LRI) system was used as a supplementary tool for the recognition of the compounds in combination with the mass spectra, and it made possible the reliable identification and accurate quantification of volatiles in chili peppers and chili-pepper-flavored olive oils.

2. Results and Discussion

2.1. Samples Analyzed

A total of seventeen fresh chili pepper samples belonging to the genus *Capsicum* were collected at the same growth phase in their full ripening stage and kindly provided by Azienda Agricola Salvadori Rita (Livorno, Italy). After their arrival, all the chili peppers were frozen until the day of the analysis and analyzed within two weeks from the freezing process. For each species, three whole chili peppers were ground together, and four homogenized samples were weighted in SPME vials, one for GC-MS and three for GC-FID analysis, assuming the analytes identified were a mean of their content in each pepper. The vials were closed and put in the fridge until the analyses, which were carried out consecutively on the same day. Three chili pepper extra virgin olive oils were purchased online. From the information reported on the label, one of them was flavored with Merkén pepper (a smoked Aji chili pepper), the second was flavored with a mix of *Capsicum chinense* peppers, and the third was flavored with the addition of a mix of different chili peppers. For convenience, the three extra virgin flavored olive oils samples were called EVOO1, EVOO2, and EVOO3, respectively. Table 1 lists the investigated samples.

Table 1. Chili peppers samples (1–17) and flavored chili pepper EVOOs (18–20) analyzed.

Sample	Chili Pepper Type	Specie	Color
1	Naga Morich	*Capsicum chinense*	Red
2	Trinidad Scorpion	*Capsicum chinense*	Red
3	Habanero Fatalii	*Capsicum chinense*	Yellow
4	Naga Yellow	*Capsicum chinense*	Yellow
5	Naga Chocolate	*Capsicum chinense*	Brown
6	Trinidad Scorpio Moruga	*Capsicum chinense*	Orange
7	Habanero Red Savina	*Capsicum chinense*	Red
8	Habanero Chocolate	*Capsicum chinense*	Brown
9	Scotch Bonnet	*Capsicum chinense*	Orange
10	Banana Pepper	*Capsicum annuum*	Yellow

Table 1. *Cont.*

Sample	Chili Pepper Type	Specie	Color
11	Terenzio	*Capsicum annuum*	Red
12	Cayenna Impala	*Capsicum annuum*	Red
13	Jalapeño	*Capsicum annuum*	Red
14	Calabrian pepper	*Capsicum annuum*	Red
15	Erotic	*Capsicum baccatum*	Orange
16	Jimmi	*Capsicum baccatum*	Orange
17	Aji	*Capsicum baccatum*	Yellow
Oil Sample	**Chili Pepper type**	**Specie**	**Color**
EVOO 1	Merkén	*Capsicum baccatum*	Yellow
EVOO 2	Mix of peppers	*Capsicum chinense*	Yellow
EVOO 3	Mix of peppers	*Unknown*	Orange

2.2. Volatile Fraction Analysis

The analyzed chili samples displayed different gas chromatography–mass spectrometry (GC-MS) chromatograms. Figures 1–3 show an example of a chromatogram for each variety. More than two hundred and fifty compounds were identified in total in the different samples, accounting for 87–91% of the total composition (Table 2 and Table S1 from Supplementary Materials). Table 2 reports volatile compounds with a percentage area greater than 0.5% in at least one of the chili peppers samples analyzed, and Table S1 from Supplementary Materials reports the other volatile compounds with a percentage area less than 0.5%.

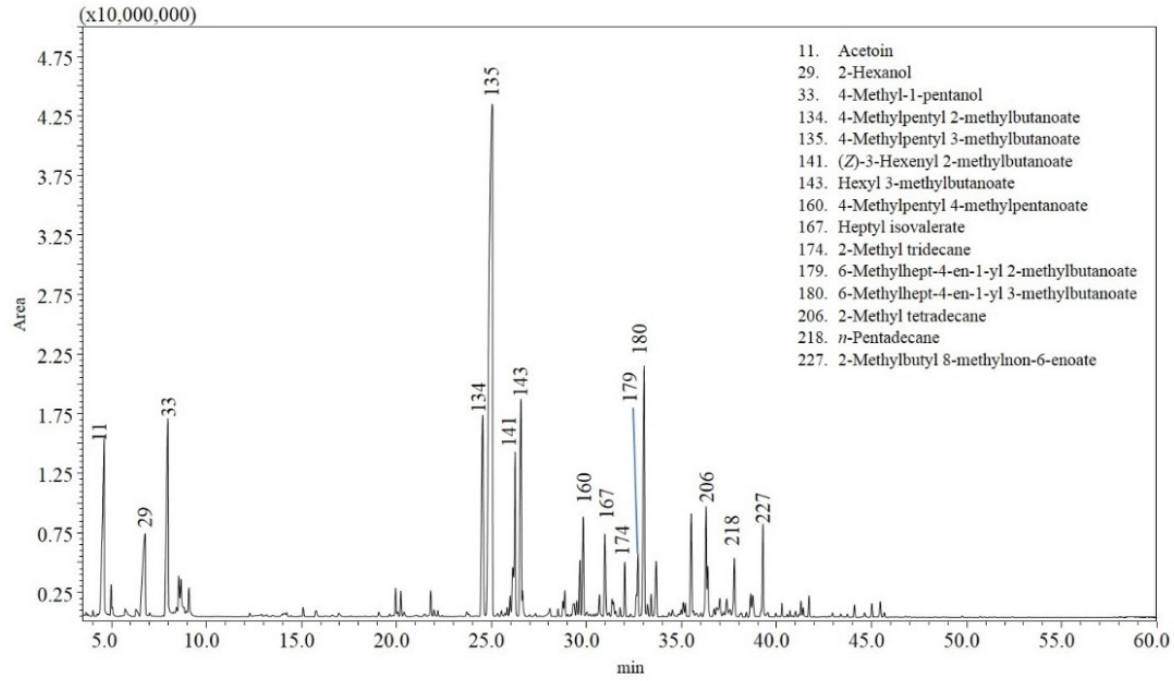

Figure 1. GC-MS analysis of the volatile profile for sample 1 (*C. chinense*—Naga Morich).

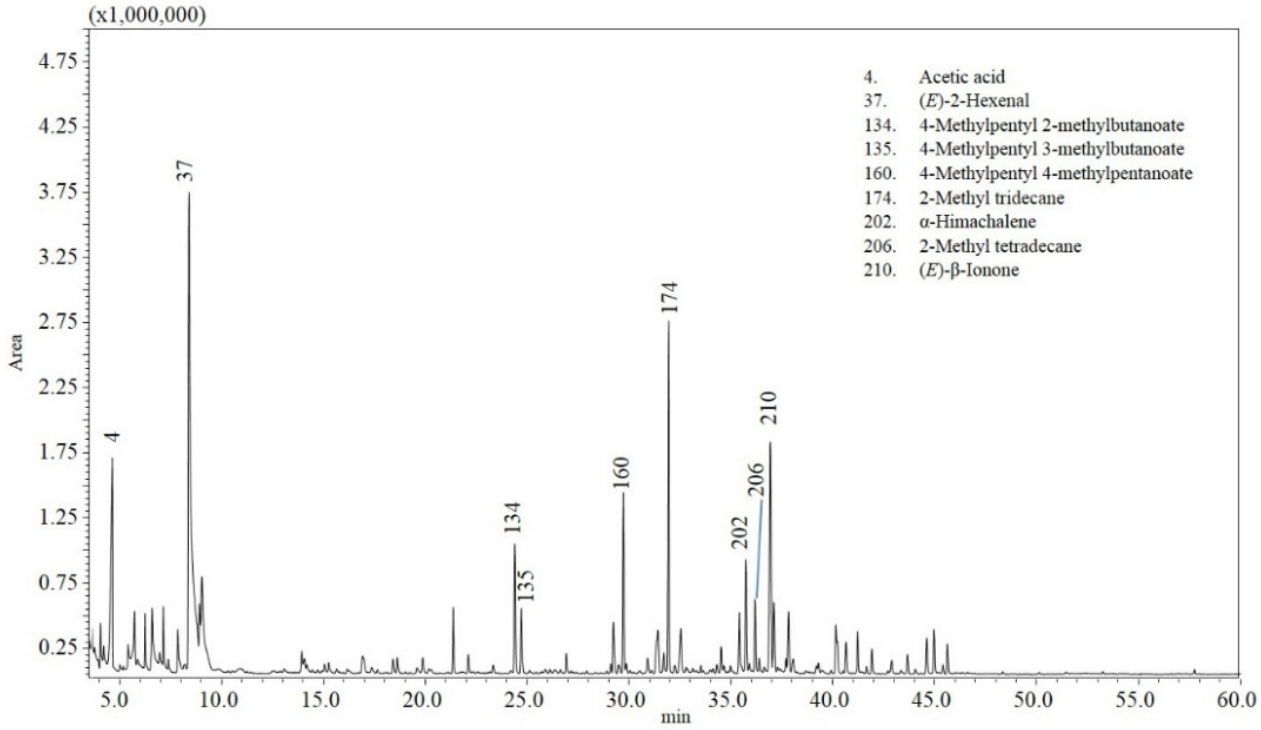

Figure 2. GC-MS analysis of the volatile profile for sample 14 (*C. annuum*—Calabrian pepper).

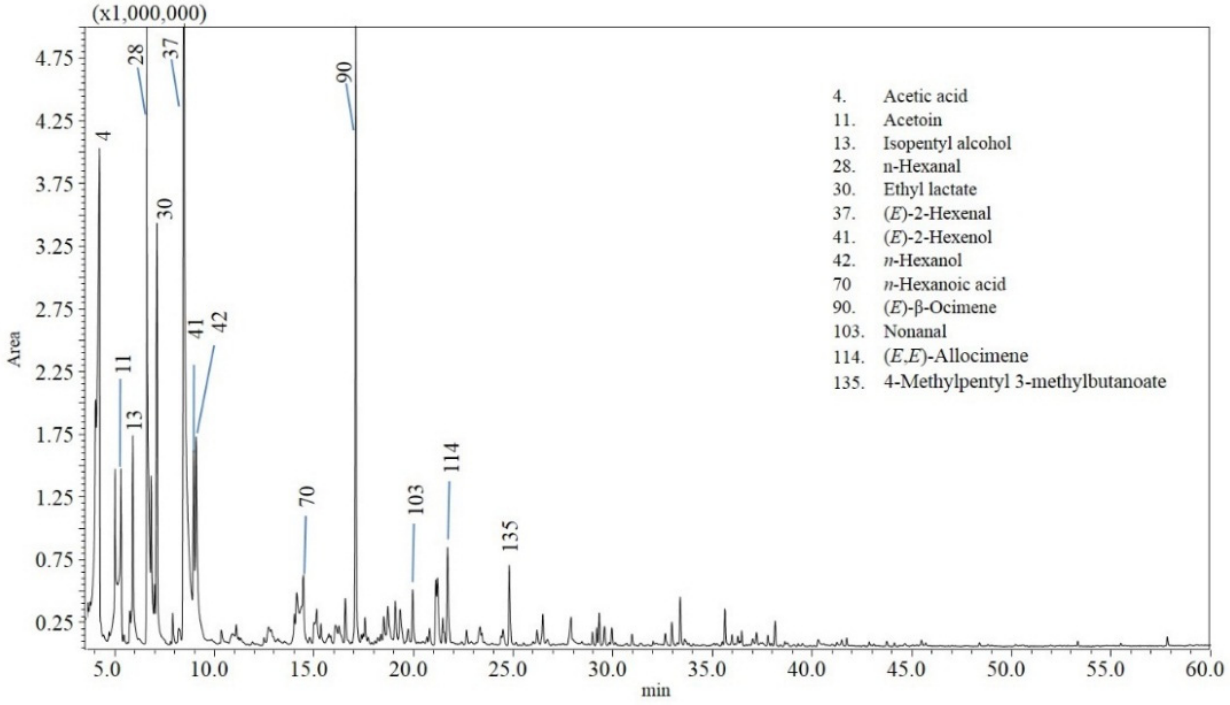

Figure 3. GC-MS analysis of the volatile profile for sample 17 (*C. baccatum*—Aji).

Table 2. Most abundant volatile compounds contained in the chili peppers samples analyzed expressed in area % as GC-FID measurement.

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum chinense*										*Capsicum annum*				*Capsicum baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
1	(*E*)-2-Butenal	619	629	0.46	0.20	0.45	0.38	0.21	0.32	0.2	0.33	0.78	0.4	0.46	1.19	1.39	0.89	0.50	0.41	0.75
2	3-methyl-2-Butanone	655	657	0.34	0.20	1.20	0.24	0.30	0.07	0.56	0.42	0.72	1.27	1.22	1.68	1.27	1.65	0.60	0.39	0.61
3	Isovaleric aldehyde	657	652	0.18	0.10	0.52	0.10	0.09	0.08	0.20	0.10	0.85	1.80	1.51	0.71	1.07	0.11	0.20	0.13	1.29
4	Acetic acid	659	661	1.02	0.09	0.25	0.77	0.30	0.59	0.39	1.14	0.60	30.41	10.5	19.29	25.97	9.46	1.26	0.97	2.38
5	2-Methylbutyraldehyde	664	662	tr	tr	0.07	tr	tr	0.14	0.15	0.06	0.13	2.08	2.97	1.64	0.62	0.25	0.37	0.09	0.06
6	Isopropyl acetate	660	650	0.06			tr	tr					0.65	0.81	0.12	0.44	0.21			0.99
7	3-Methyl-2-butanol	668	674	tr	tr		0.08	tr	tr		0.08	0.12	0.51	0.63	0.52	0.59	1.40	0.81		0.12
8	(*Z*)-2-Buten-1-ol	673	671	tr	tr		tr	tr		0.18	0.12	0.54	0.19	0.28	0.35	0.56	0.26	0.08	1.23	1.61
9	3-Penten-2-one	690	691	tr	tr	0.10	tr	tr	tr	0.13	0.08	0.18	1.99	0.24	0.85	0.12	0.13			4.25
10	Propionic acid	703	698	0.21		0.07	0.06		tr		0.74	0.22	0.70	1.86	0.48	0.19	0.35	0.19	0.06	0.23
11	Acetoin	726	716	1.40	0.10	0.07	0.27	0.13	0.11	0.09	0.59	4.55	17.53	6.16	11.88	13.88	3.65	0.42		0.55
12	Isoprenol	729	724	tr	tr	0.06	tr	tr	0.11	tr	tr	0.20	1.35	3.13	0.44	0.22	0.05	0.18	0.23	0.25
13	Isopentyl alcohol	733	729	0.09	tr	tr	tr	tr	0.05	1.06	0.79	0.25	1.30	1.25	1.12	0.83	0.32	0.29		1.95
14	sec-Butylcarbinol	738	733	tr	tr	tr	tr		0.07	0.65	0.15	0.19	0.95	0.85	1.18	1.78	0.33			0.11
16	Isopropyl ethyl ketone	745	742	tr	tr	0.06	0.07	tr	tr	0.14	0.11			1.16		0.23	0.26		0.07	
17	Ethyl isobutanoate	754	754	tr	tr	0.06	tr	tr	0.1	0.20	0.5	0.44	0.29	2.08	1.40	0.14	0.32	0.32	0.12	0.18
18	Isobutyric acid	761	774	tr	tr	tr	tr	tr		0.11	0.05	0.52	1.11	0.16	0.72	0.06	0.05		0.12	tr
19	Toluene	764	763					tr			0.24			0.38	0.54	0.20	tr	1.70		0.37
20	Pentyl alcohol	763	763	0.07	tr	tr	tr	tr	0.18	1.44	0.74	0.26	0.16	0.28	0.39	0.15	0.84	0.20	0.17	0.26
21	(*E*)-2-Penten-1-ol	766	761	0.12	tr	0.06	tr				1.03	0.36	0.21	0.61	0.53	0.35	0.28		0.32	tr
22	Prenol	770	772	tr	tr	tr	tr	tr	0.07		0.39	0.27	0.30	0.30	0.30	0.16	0.06	0.33	0.16	0.72
23	2,3-Butadienol	788	788	0.10		tr	tr	tr			0.22	0.41	0.05	0.26	0.65	0.18	0.34	1.63	0.06	0.48
24	3-Methylcrotonaldehyde	787	780		tr	tr	tr	tr				0.20	0.11	tr	0.62	0.21				0.05
25	Isopentyl formate	788	791			tr	tr	tr		0.38				0.23	0.28					0.60
27	(*Z*)-3-Hexenal	798	797		tr	tr			tr	tr	0.45	1.46	0.12	0.23	0.63	0.39				
28	*n*-Hexanal	801	801	tr	tr	0.06	tr	tr	tr	tr	0.85	0.79	2.15	2.35	2.25	3.44	3.74	16.26	20.74	16.38
29	2-Hexanol	806	802	1.43				tr	tr	tr	0.75	0.50	0.29	1.32	1.63	0.19		4.47		0.27
30	Ethyl lactate	806	814					tr	tr		0.22	0.21	0.47	0.12	0.39	0.20		0.98	0.71	1.37
31	4-Methyl-2-pentenal	816	814			tr	tr	tr	tr	tr		0.53	0.11	0.37	0.32	0.65	1.32	2.75	1.46	2.04
33	4-Methyl-1-pentanol	838	832	2.72	0.44	0.67	0.40	0.51	1.37	23.15	13.61	2.48	2.03	2.72	1.41	1.59	0.52	0.21	0.19	0.35
35	Ethyl 2-methylbutanoate	846	842	0.06	tr	0.13	0.11	tr	0.11	2.86	0.79	0.49	0.4	0.36	0.16	0.23	0.27			0.14
37	(*E*)-2-Hexenal	850	850				tr		0.09	0.61	19.38	0.59	8.05	29.8	2.46	6.57	26.85	43.22	34.59	21.58
38	(*E*)-3-Hexenol	854	847	0.50	0.53	0.25	0.50	0.49	0.55	6.07	0.68		0.33		0.15	0.88	8.99		3.36	
39	(*Z*)-3-Hexenol	856	856	0.32	0.31	0.15	tr	0.21		2.11	0.54		0.36							

Table 2. *Cont.*

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum chinense*										*Capsicum annum*				*Capsicum baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
40	Isovaleric acid	838	842	0.11	0.11	0.18	tr	0.05	0.38	0.63	0.41	0.21	0.61	0.87	0.20	1.01	0.77			
41	(*E*)-2-Hexenol	864	864	0.09		0.07	tr	tr		0.36	2.80		1.04	2.89	0.19	3.08	2.91	1.07	1.58	1.90
42	*n*-Hexanol	868	867	0.37	0.74	0.12	0.3	0.57	0.25	2.92	1.89	0.26	0.91	2.74	0.42	1.45	3.22	7.53	3.63	2.44
43	2-Methylbutyric acid	883	881	tr	tr	tr	tr	tr	tr	0.27	0.07	0.11			0.22	0.65	0.63	tr	0.46	0.14
44	*n*-Pentanoic acid	889	918	tr	tr	tr	tr	tr	tr	0.10		0.09	0.20	0.60	0.23	0.44	0.12	tr		tr
60	3-Methyl-ethylpentanoate	962	953	tr	tr	tr	tr	tr	tr	0.64		0.86	0.06	tr	tr	0.10	tr		0.25	tr
69	6-Methyl-hept-5-en-2-one	984	986	tr	tr	0.06	tr	tr	0.07	tr	0.06	0.52	0.48	0.21	0.31	0.57		0.11	0.18	0.46
70	*n*-Hexanoic acid	989	997	tr	tr	0.10	tr	tr	tr	0.07	0.07	0.71	0.34	0.14	0.24	0.67	0.42	0.51	0.36	0.08
71	Ethyl hexanoate	998	1003	tr	tr	0.12	0.06	tr	tr	tr	0.58		0.68		0.08	tr	tr	0.35	0.89	0.52
80	*p*-Cymene	1025	1024	tr	tr	tr	tr	tr	tr	tr	0.33	0.6	0.07	0.15	0.12	0.06	tr	tr	0.33	0.05
81	Limonene	1028	1030	tr	0.06	tr	tr	tr	tr	0.07	0.31	1.05	0.06	0.22	0.55	0.41	tr	0.08	0.18	0.43
84	(*Z*-β-Ocimene	1035	1035	tr			tr		tr	tr	tr	0.23	tr	tr	tr	tr	tr	tr		0.64
90	(*E*)-β-Ocimene	1046	1046		tr			tr		0.17	0.05	0.97	0.96	0.3	0.32	0.24		2.55		9.70
91	Isopentyl butanoate	1048	1050		tr	tr	0.05	tr	tr	0.14	0.3	0.05		tr		1.08	0.06	0.05	0.06	0.06
94	(*E*)-2-Octenal	1067	1058	tr	tr	tr	tr	tr	tr		0.72	0.09	0.17	0.06	0.11	0.07	tr	0.06	0.07	tr
98	Guaiacol	1086	1094	tr		tr	tr	tr	tr	tr	0.13	0.70	tr	tr		0.07	tr	0.10	0.38	0.52
99	Isobutyl tiglate	1091	1093	tr	tr	tr	tr	tr	tr	0.08	tr	0.20	0.12	tr	1.13	0.20	tr	0.19	0.34	0.64
100	3-Methylbutyl 2-methylbutanoate	1098	1104	tr	tr	tr	tr	tr	0.22	tr	0.19		0.10		0.13	tr		0.09	tr	0.54
101	Linalool	1098	1101		tr	tr	tr	tr						0.30	0.83	0.17	0.06	0.08	0.19	tr
103	*n*-Nonanal	1103	1107	tr		tr	tr	tr		tr	tr	0.47	0.11	0.18	1.33	0.25	0.25		0.21	0.75
104	3-Methylbutyl isovalerate	1104	1109	0.26	0.07	0.29	0.29	0.09	0.92	0.25	0.35	0.86	0.27	0.29		0.67				
105	2-Methylbutyl isovalerate	1106	1109	tr		tr	tr	tr	0.15	tr	0.65		tr		0.09	tr	0.11		tr	tr
106	3-Methylpentyl isobutanoate	1110	1115	0.15	tr	0.29	0.15	0.06	0.32	2.08	0.05	0.21	0.06	0.06	0.70	0.57	tr	tr	0.47	tr
107	Isohexyl isobutanoate	1112	1110	tr	0.75	tr	tr	tr	tr	tr	0.09	0.79	tr	0.22	0.12	0.14	tr	0.07	tr	tr
111	(4*E*,6*Z*)-Alloocimene	1128	1128	tr		tr			tr	tr		0.07			0.07	0.09	tr	0.13	tr	0.90
112	2-Vinylanisole	1130	1135						tr	tr	tr	0.08	tr	tr		0.09		0.15		0.87
114	(*E*,*E*)-Allocimene	1140	1145					tr				0.11		0.05		0.06	tr	0.21	0.08	1.33
116	Pentyl isovalerate	1142	1143	0.34	0.18	0.23	0.64	0.08	1.08	0.21	0.27	0.07	tr		0.10					tr

Table 2. *Cont.*

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum chinense*										*Capsicum annum*				*Capsicum baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
117	Hexyl isobutanoate	1146	1150	tr	0.54	0.13	0.13	0.06	0.12	0.25	0.05	0.14	tr	0.06	0.14		tr			tr
125	3-Methoxy-2-isobutylpyrazine	1175	1176							tr	0.06	0.52	0.19	tr	1.74	0.07	tr	tr	0.50	
134	4-Methylpentyl 2-methylbutanoate	1198	1202	6.54	3.14	2.41	2.33	1.08	9.80	13.21	12.86	4.58	1.31	1.40	1.23	1.12	2.95	0.05	0.13	0.31
135	4-Methylpentyl 3-methylbutanoate	1209	1206	33.12	21.11	16.02	21.67	13.98	32.8	22.69	16.65	20.13	2.32	1.44	2.21	1.42	1.52	0.62	0.76	1.16
138	Citronellol	1222	1232	0.11		tr	0.07	1.99	tr	tr	0.11	0.07	tr	tr	tr	tr	tr	tr		tr
140	ESTER	1229		0.78	1.19	0.55	0.64	0.74	0.25	0.32	1.17	0.12	0.07	tr	0.11	tr	tr	tr	tr	0.16
141	(*Z*)-3-Hexenyl 2-methylbutanoate	1233	1231	2.41	4.79	2.36	1.34	2.02	1.59	1.64	0.89	0.48	tr	0.05	0.20	0.05	tr	tr	tr	tr
142	(*Z*)-3-Hexenyl 3-methylbutanoate	1237	1243	1.02	2.92	1.42	7.74	1.50	9.55	0.96	0.57	0.65	tr	0.05	0.17	0.11	tr	tr	0.05	0.31
143	Hexyl 3-methylbutanoate	1246	1243	4.02	7.88	4.57	12.34	8.87	7.77	0.16	0.09	0.17	tr	tr	0.10	tr	tr	tr	0.12	tr
144	(E)-Hex-2-enyl 3-methylbutanoate	1248	1243	0.37	0.45	0.18	0.32	0.96	1.14	tr	tr	0.06		tr	0.12	tr	0.21	tr	tr	tr
145	Heptyl isobutanoate	1251	1248	tr	0.80	0.21	0.17	tr	0.07	tr	tr	tr		tr	0.09	tr	tr	tr		tr
151	6-Methylhept-4-en-1-yl isobutanoate	1289	1293	0.15	1.39	0.79	0.09	0.99	0.05	0.05	tr	0.09	tr	tr	0.08			tr		tr
152	3-Methylpentyl (2*E*)-2-methyl-2-butenoate	1291	1300	0.5	0.39	0.17	0.39	0.2	0.47	0.14	1.77	0.22			0.09	tr	tr	tr		0.05
155	5-Methylhexyl 3-methylbutanoate	1300	1303	0.14		0.21	0.35		tr	0.06	0.82	1.86	1.09	0.54	2.39	0.31	0.62	0.08	0.19	0.20
157	ESTER	1302		0.17	0.23	0.07	0.13		0.17	0.11	0.66			tr		tr				
158	Heptyl butanoate	1308	1298	0.18	0.24	0.41	1.16	0.31	0.15	0.10	0.12					tr				tr
159	4-Methylhexyl 2-methylbutanoate	1308	1307	0.87	0.62	0.33	0.12	0.12	0.44	0.38	0.27	0.12	0.06		0.11	0.10	tr		0.05	
160	4-Methylpentyl 4-methylpentanoate	1313	1315	1.63	1.09	1.02	0.64	0.76	0.46	0.60	0.53	0.27	tr	0.07	0.08	tr	2.02	tr	tr	tr
165	Heptyl 2-methylbutanoate	1332	1333	0.31	1.45	0.59	0.66	0.91	0.14	tr	tr	0.29	tr		tr	tr				tr
167	Heptyl isovalerate	1338	1338	1.67	4.97	3.38	4.09	5.50	0.46	0.13	0.08		tr	tr	0.26	tr	tr	tr	0.05	0.11
170	α-Cubebene	1347	1347	0.68	0.31	tr	0.69	0.48	0.21	0.06		0.09	tr	tr	0.08	tr		tr	0.07	
171	ESTER	1352		0.24	0.75	0.3	0.39	0.57	0.12	0.1	tr	0.09		tr	0.07	tr				tr

Table 2. *Cont.*

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum chinense*										*Capsicum annum*				*Capsicum baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
172	α-Longipinene	1354	1352	0.08	0.06	0.34		0.35	tr	0.05	tr	1.57		tr		0.09	1.01			tr
174	2-Methyl tridecane	1362	1365	1.54	0.21	0.19	0.31	0.16	0.16	0.05	0.07	1.26	0.05	0.21	0.53	0.33	3.28	tr	0.28	tr
176	α-Ylangene	1372	1371	0.09	tr	tr	tr	1.43	0.07	tr	-			tr	0.06		tr	tr		tr
177	Cyclosativene	1370	1367			tr	tr			tr	0.05	0.58	0.06	tr	0.17	tr		tr		tr
178	α-Copaene	1376	1375	tr	0.73	tr	0.73		0.06	0.08	0.27		0.18	0.34	1.83	0.56	0.65	tr	0.36	0.09
179	6-Methylhept-4-en-1-yl 2-methylbutanoate	1378	1383	1.72	1.61	2.02	1.45	16.3	0.44	0.05	0.09	10.37				1.84	0.07		0.56	tr
180	6-Methylhept-4-en-1-yl 3-methylbutanoate	1385	1388	7.77	14.12	11.67	14.45	16.15	1.13	0.81	tr	0.34		0.05	0.19	1.76	tr	tr	tr	0.22
181	β-Elemene	1389	1390	0.22	tr	0.09			0.08	tr		0.59	tr	0.31	0.29	0.19	0.38	0.28	9.36	tr
182	Sativene	1392	1394						tr	tr	tr	0.22	0.07	tr	0.13	0.61		tr		
183	6-Methylheptyl 2-methylbutanoate	1394	1398	0.43	0.77	0.64	0.36	0.57	0.24	tr	tr					tr	tr	tr		0.16
186	6-Methylheptyl 3-methylbutanoate	1399	1402	1.53	1.75	2.10	1.15	3.16	tr	tr	-	0.13				tr	tr	0.06	tr	tr
192	(*E*)-α-Ionone	1421	1421		0.11		0.30	0.24	0.13	tr	tr			tr	0.09		tr	0.52	0.96	
196	(*E*)-α-Bergamotene	1435	1432	tr				0.20	tr	tr	tr			tr		1.12	0.07			tr
197	6-Methyl-4-heptenyl pentanoate	1436	1438	0.09	0.55	0.50	0.60	1.21	0.09	tr	0.16							tr		tr
198	Octyl isovalerate	1437	1441	0.31	0.81	0.58	0.58	1.55	tr	tr	-			tr	tr	tr				tr
199	ESTER	1443		4.19	1.83	0.84	1.10	0.68	0.74	0.11	0.16	1.57	tr	0.20	0.26	0.14	0.51	tr	0.13	tr
200	(*E*)-Geranylacetone	1446	1450	0.10	0.23	0.16	0.06	0.23		tr	tr	0.74	tr	tr	0.11	0.08	tr	tr	0.10	0.27
202	α-Himachalene	1450	1449	0.12	0.10	0.83	tr	0.26			0.45					0.17			0.23	
206	2-Methyl tetradecane	1462	1463	1.11	0.67	1.08	0.77	0.05	0.42	0.07	0.22	1.39	0.09	0.21	0.27	0.11	1.04	tr	0.14	tr
207	Oxacyclododecan-2-one	1467		0.44	0.24	0.93	2.78	0.05	0.09	tr	tr				0.16	tr	0.08		0.09	0.06
210	(*E*)-β-Ionone	1482	1482	0.35	0.74	0.15	0.24	0.14	0.40	0.09	0.06		tr	tr	0.09	0.18	0.21	tr	0.17	tr
211	γ-Himachalene	1483	1481	0.35	0.99	4.74	0.27	0.60	11.64	tr	1.07	1.84	tr	tr	0.09	tr	tr	tr		tr
212	β-Chamigrene	1484	1479	0.41	tr	tr	0.05	0.13	0.30	tr	0.20	0.57	0.06	tr	0.97	0.11	1.40	tr	0.60	
213	6-Methylhept-4-en-1-yl 2-methylbutanoate	1478	1481	0.18		0.32	tr	2.08						0.26	tr	0.22	0.14			0.07
214	Isobutyl 8-methylnon-6-enoate	1488	1496	0.33	0.71	3.36	0.35	0.25	0.10	tr	tr	0.09		tr	0.24	tr	tr	tr	0.86	0.05
217	α-Selinene	1496	1501	0.14	0.50	tr	tr	0.27	0.06	tr	tr					tr			0.78	
218	*n*-Pentadecane	1498	1500	0.54	0.86	0.57	0.39	0.06	0.38	0.06	0.09	0.53	0.06	0.13	0.23	tr	0.05	tr		0.07

Table 2. *Cont.*

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum chinense*										*Capsicum annum*				*Capsicum baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
219	α-Cuprenene	1501	1508	0.08	tr	0.18	0.11	0.10	0.57	tr	0.21	0.28	0.21	0.15	0.06	0.32	0.31	0.13	0.28	tr
220	Isobutyl 8-methylnonanoate	1502	1496	0.07	0.08	0.39	tr	tr	tr	0.10	tr	1.18			0.74	tr	0.10		tr	0.11
223	δ-Cadinene	1519	1518	0.76	0.59	0.22	0.54	0.30	0.19	tr	tr	0.06		tr	0.10	tr	tr	tr	0.11	tr
227	2-Methylbutyl 8-methylnon-6-enoate	1537	1545	2.14	4.02	6.35	1.19	0.42	0.31	tr	tr		tr	tr	0.11	tr	0.25			tr
235	Dendrolasin	1570	1573	0.24	0.28	0.06	0.55	tr	tr			0.14		tr	0.39	tr	0.09			
237	(*E*)-2-Tridecen-1-ol	1583	1573	0.16	0.15	0.53	0.10	0.16	tr	tr										tr
238	Isopentyl 8-methylnon-6-enoate	1586	1592	0.36	0.27	0.89	0.26	0.96	tr	tr	tr	0.15		tr	0.06	tr	0.80	tr	tr	tr
249	Cadalene	1675	1677	0.12	tr	tr	tr	0.05	tr	tr	tr			tr	0.16	tr	1.40	tr	tr	tr
250	4-Methylpentyl 8-methylnon-6-enoate	1685	1692	0.35	0.28	2.22	0.18	0.15	0.09	tr	tr	0.26				tr	0.19			tr
252	4-Methylpentyl 8-methylnonanoate	1702	1710	0.09	0.07	0.63	0.08	0.05	0.06	tr	0.07	0.08		tr	0.16	0.07	tr	tr		tr
261	ESTER	1852		tr	tr	0.82	tr	tr	tr											
	Total			**91.72**	**91.47**	**84.21**	**88.88**	**92.44**	**90.91**	**91.1**	**94.34**	**82.04**	**89.73**	**89.35**	**80.53**	**87.97**	**90.8**	**92.04**	**92.17**	**85.31**

The compound's number is reported in order of elution, considering the total number of compounds eluted. For the identification of the compounds not reported in this table, see Table S1 from Supplementary Materials. tr = trace compound.

Volatile organic compounds (VOC) are commonly correlated with food flavor and fragrance, and their determination is important to evaluate food quality, authenticity, purity, and origin [9]. Methyl and ethyl esters, for example, provide strong fruity notes in foods, whereas terpenes provide woody, floral, fruity, and spicy notes. Aldehydes have a low odor threshold, and the sniffing analysis of *Capsicum* reported their presence as green, cucumber, pungent, or herbaceous odor notes [10,11].

In addition, it has been proven that the volatiles' profile of *Capsicum* is mainly affected by varieties [5], ripening stages [3], and processing [12].

The analyses carried out on *Capsicum chinense* peppers revealed that the most relevant compounds are esters (4-methylpentyl 3-methylbutanoate, 6-methylhept-4-en-1-yl 3-methylbutanoate, 4-methylpentyl 2-methylbutanoate, hexyl 3-methylbutanoate, (*Z*)-3-hexenyl 2-methylbutanoate, 2-methylbutyl 8-methylnon-6-enoate, 6-methylhept-4-en-1-yl 2-methylbutanoate, heptyl isovalerate, 4-methylpentyl 4-methylpentanoate, 6-methylheptyl 3-methylbutanoate, and (*Z*)-3-hexenyl 3-methylbutanoate) (Figure 1).

The presence of several aliphatic esters in the *C. chinense* variety has been reported in the literature [3–6]; it has been confirmed that esters, especially straight-chain esters, are generally metabolized from fatty acids through oxidation [13], and that branched saturated and non-saturated esters can be derived from amino acids' metabolism [5].

Among the analyzed *C. chinense* samples, Habanero red savina, Habanero chocolate, and Scotch bonnet showed a lower content of esters and a greater amount of alcohols and aldehydes (Figure 4). It has been demonstrated that ester biosynthesis is limited by alcohol concentration, which can modify the content of esters in specific cultivars [14]. In the analyzed species, even if there is good alcohol availability, the production of the esters is probably inhibited by the absence of free fatty acids.

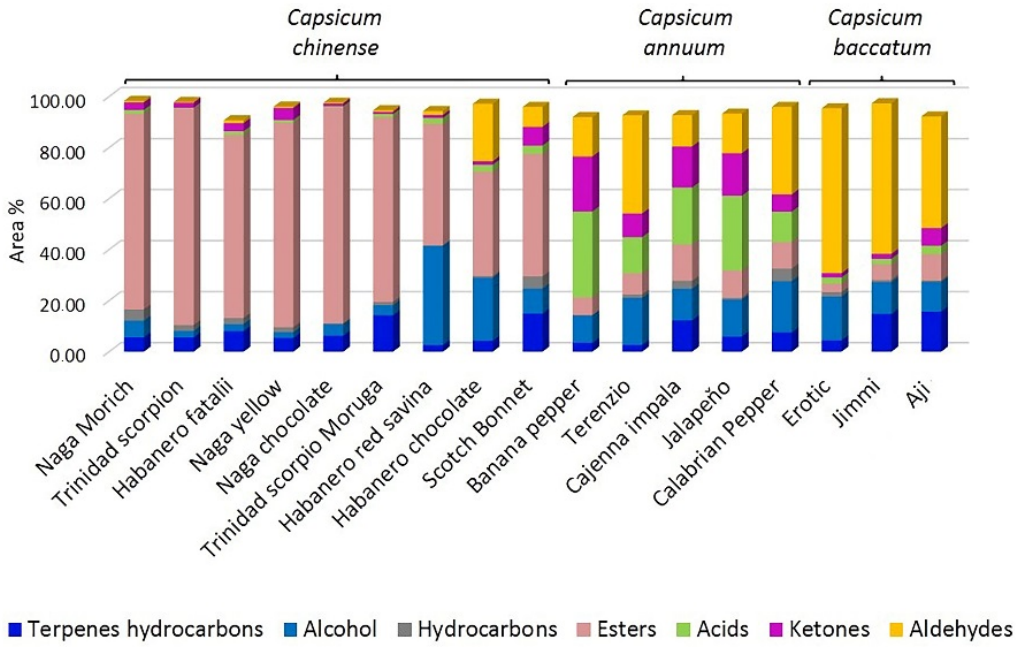

Figure 4. Distribution of volatile compounds' class identified in the analyzed samples.

Literature data on the *Capsicum Chinese* variety [3,4] report the presence of a little amount of 2-isobutyl-3-methoxypyrazine in the Habanero peppers variety (0.01 mg kg^{-1}). Effectively, the three Habanero chili peppers analyzed in the present study did not present this compound (Habanero fatalii (sample 3) and Habanero red savina (sample 7)), or had a very little quantity (Habanero chocolate (sample 8) (0.06%)) of 2-isobutyl-3-methoxypyrazine, which was mainly detected in the Scotch Bonnet variety (sample 9) (0.52%).

The volatile profile of the analyzed *Capsicum annuum* samples was principally characterized by acids, in particular acetic; aldehydes ((*E*)-2-hexenal, *n*-hexanal, 2-methylbutyraldehyde,

and isovaleric aldehyde); ketones (acetoin and 3-methyl-2-butanone); alcohols (4-methyl-1-pentanol and isoprenol); and esters (4-methylpentyl 3-methylbutanoate and 4-methylpentyl 2-methylbutanoate) (Table 2 and Table S1 and Figures 2 and 4).

Terenzio and Calabrian pepper varieties showed a greater abundance of (*E*)-2-hexenal than the others belonging to the same species. Only the Jalapeňo pepper contained 6-Methylhept-4-en-1-yl 2-methylbutanoate and 6-Methylhept-4-en-1-yl 3-methylbutanoate.

Banana and the Jalapeňo chili pepper showed the highest amount of acids, followed by Cayenna impala, Terenzio, and Calabrian varieties.

Regarding alcohols, the Calabrian pepper is the only one distinguished by a great percentage of (*E*)-3-hexenol (8.99%).

Concerning terpenoids, the Banana pepper showed the highest amount of (*E*)-β-ocimene, which is absent in the Calabrian pepper. The latter, however, has a higher content of α-longipinene, which is absent in Banana and Cayenna pepper varieties. The Cayenna pepper presented a high amount of α-copaene and β-chamigrene. The latter was also found in larger amounts in the Calabrian pepper. The Jalapeňo chili pepper is the only one with an amount of (*E*)-α-bergamotene greater than 1%.

Furthermore, the Cayenna Impala variety presented a higher amount of 2-isobutyl-3-methoxypyrazine than the other samples. This compound was found to possess an extremely potent odor (odor threshold of 2×10^{-6} mg kg^{-1}), similar to that of fresh green bell peppers [15].

Regarding *Capsicum baccatum* chili peppers, a great contribution to the volatile profile is given by alcohols (*n*-hexanol, (*E*)-3-hexenol, (*E*)-2-hexenol, (*Z*)-2-buten-1-ol); aldehydes ((*E*)-2-hexenal, *n*-hexanal, 4-methyl-2-pentenal); and esters (ethyl hexanoate, isobutyl 8-methylnon-6-enoate, 4-methylpentyl 3-methylbutanoate, 4-methylpentyl 3-methylbutanoate, ethyl lactate) (Table 2, Table S1 and Figure 3).

The Aji variety has higher ketones, esters, and terpenes contents than the other chili peppers of the same species. The high percentage area encountered for terpenes, ketones, and esters is relative to (*E*)-β-ocimene, 3-pentenone, and isopropyl acetate, respectively. The Erotic and Jimmi varieties are similar in respect to the amount of aldehydes, ketones, and hydrocarbons identified.

Compounds, such as α-ionone and β-ionone, which may be formed by oxidative degradation of δ-carotene, β-carotene, and terpenoids [16], were particularly found in orange peppers belonging to this third species.

Although the literature reports several studies on the aroma and the content of capsaicinoids in chili peppers [17], to the best of our knowledge, capsaicinoids [18,19] and the volatile profile of chili-pepper-flavored extra virgin olive oil have not been investigated well [19]. For this reason, a study on the aroma profile of flavored EVOOs was carried out and compared to that of fresh peppers and unflavored olive oils. Table S2 reports the results of the volatile compounds identified in the flavored olive oils.

2.3. Statistical Analysis

PCA was performed on the 118 most abundant volatile compounds identified in chili peppers (Figure 5A) and on the same numbers of volatiles, also including the data acquired for chili-pepper-flavored extra virgin olive oils (Figure 5B). For statistical data treatment, the following conditions were applied: original values are ln(x)-transformed; rows are centered; Pareto scaling is applied to rows; SVD with imputation is used to calculate principal components.

As shown in Figure 5A, the PCA score plot in the space of the two PCAs explains 56.0% of the total variance, only considering the peppers, and 49.0% of the total variance, also considering the oils (Figure 5B). This confirms the applicability of the built model and the other unknown samples. From Figure 5, it is clear that at positive values of PC1 and negative values of PC2, the *Capsicum baccatum* species is well separated, whereas the *Capsicum annuum* is present at negative values of PC1 and PC2. Furthermore, the *Capsicum chinense* species is separated well on PC1 in the positive region. As far as the PC2 shown

in Figure 5B is concerned, it is interesting to notice that the extra virgin olive oils EVOO1 (containing Merkén pepper, a smoked Aji chili pepper belonging to *Capsicum baccatum*) and EVOO2 (containing a mix of the *Capsicum chinense* pepper) are correctly grouped with the peppers used as a flavoring in the producing process. Since the EVOO3 samples were flavored with a mix of *Capsicum* belonging to different species, it is not possible to insert them into a specific group. Table S4 from Supplementary Materials lists the compounds that mainly influence the plot and their contribution to PC1 and PC2.

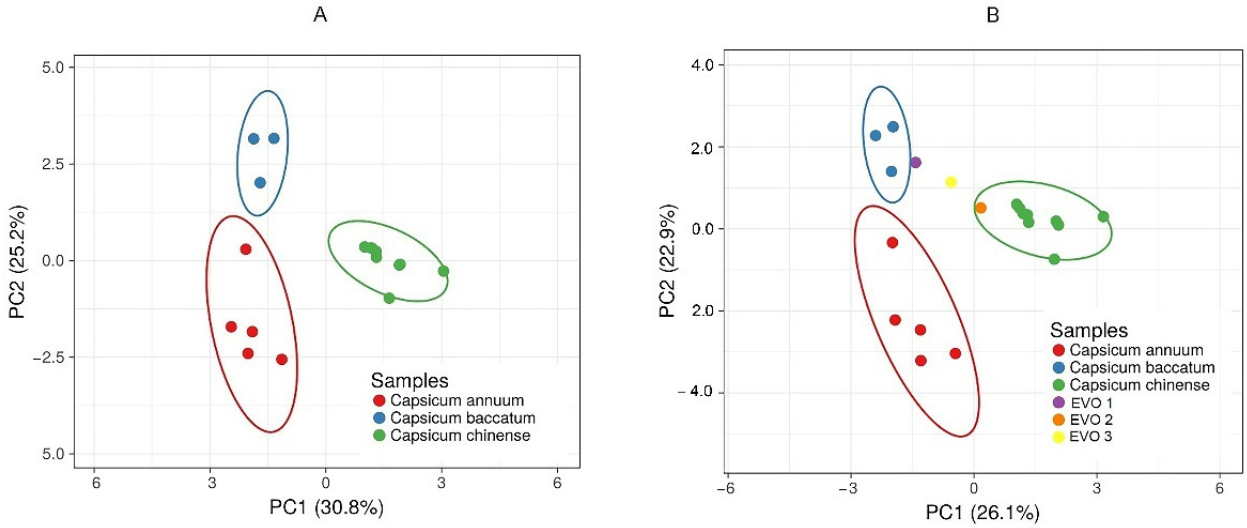

Figure 5. PCA analysis based on relative percentage areas of the 118 most abundant identified volatiles in chili peppers (**A**) and in chili peppers compared with chili-pepper-flavored extra virgin oils (**B**). *X* and *Y* axis show principal component 1 and principal component 2, which explain (**A**) 30.8% and 25.2% of the total variance and (**B**) 26.1% and 22.9% of the total variance, respectively. Prediction ellipses are such that with probability of 0.95, a new observation from the same group will fall inside the ellipse. $N = 19$ data points.

Hierarchical cluster analysis (HCA) was performed using both the relative percentage area of the class of the compound identified (Figure S1 from Supplementary Materials) and the relative percentage area of the most abundant volatiles (118) (Figure S2 from Supplementary Materials).

The cluster analysis based on the identified compounds class showed an overlap between the different species; consequently, it is not possible to distinguish between different *Capsicum* species by only considering their contribution (Figure S1 from Supplementary Materials).

The cluster analysis based on the patterns of the most abundant volatiles instead showed good separation of *C. chinense* from the *C. annuum* and *C. baccatum* group (Figure S2 from Supplementary Materials).

In accordance with PCA analysis, HCA built by introducing the volatile patterns of the three flavored olive oils shows the EVOO2 sample grouped with *Capsicum chinense* peppers and EVOO1 grouped with the *Capsicum baccatum* species, confirming the goodness of the model (Figure 6). In addition, the results confirm the information on the labels of EVOO1 and EVOO2 and guarantee the quality of commercial products, confirming the usefulness of the model for this purpose.

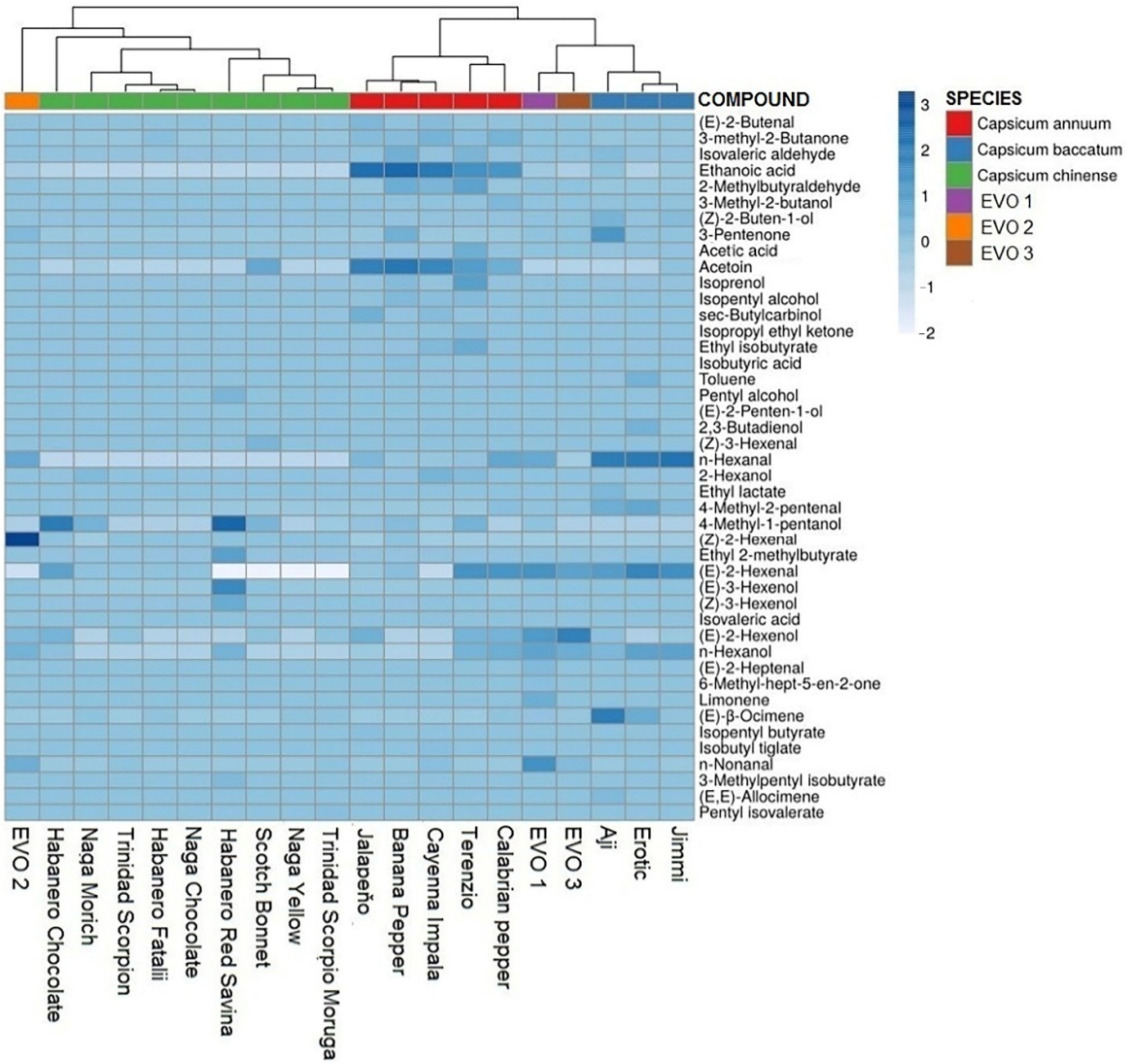

Figure 6. Hierarchical cluster analysis based on relative percentage areas of the 118 most abundant identified volatiles. Original values are ln(x + 1)-transformed. Rows are centered; Pareto scaling is applied to rows. Imputation is used for missing value estimation. Columns are clustered using correlation distance and average linkage. There is a total of 44 rows and 20 columns.

2.4. Sensorial Analysis

With regard to the aroma, the sensorial test revealed a wide range of odor impressions in the 17 varieties of chili peppers examined.

The chili peppers belonging to the *C. chinense* species were mainly characterized by exotic, fruity, and/or sweet notes (Figure 7 and Figure S3 from Supplementary Materials), and their aromas were the most intense among all samples investigated. Such notes are due to the presence of numerous esters, especially 4-methylpentyl 3-methylbutanoate and 4-methylpentyl 2-methylbutanoate [20], Hexyl 3-methylbutyrate, (*Z*)-3-Hexenyl 3-methylbutyrate, and (*Z*)-3-Hexenyl 2-methylbutyrate. The dairy, buttery, and creamy notes found in some peppers, such as Naga morich, Habanero fatalii, Naga chocolate, Trinidad scorpio moruga yellow, Habanero red savina, Scotch bonnet, and Habanero chocolate, are due to the presence of some ketones such as acetoin [21,22], and especially medium-short chain fatty acids such as *n*-decanoic, which characterizes the base note of the Habanero fatalii.

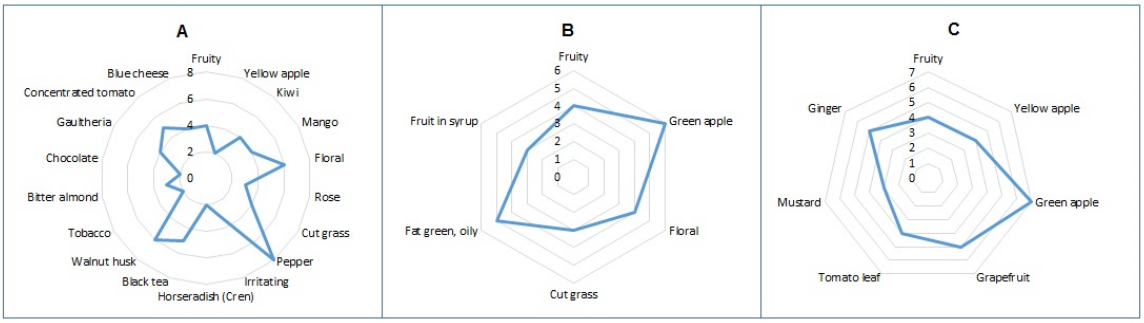

Figure 7. Aroma profile of three different species of pepper chosen as example from descriptive sensory analysis on line scale (n = 10). Panel (**A**) shows sample 1 (Naga Morich, *Capsicum chinense*); panel (**B**) shows sample 14 (Calabrian pepper, *Capsicum annuum*); and panel (**C**) shows sample 17 (Aji, *Capsicum baccatum*).

The sweet note of vanilla perceived in the Scotch Bonnet is confirmed from an analytical point of view by the presence of guaiacol, a compound that characterizes the vanilla beans [21,22].

Similarly, the note of "wintergreen" (*Gaultheria procumbens*) found in the Scotch Bonnet and Habanero Fatalii is confirmed by the presence of methyl salicylate in the volatile profile [21,22].

In contrast, *C. annuum* and *C. baccatum* showed different intensity and aroma profiles with a medium-intense mixture of fruity and vegetable-like notes (Figure 7 and Figures S4 and S5 from Supplementary Materials) due to the presence of (*E*)-2-hexenal in both species, and also depending on isopentyl alcohol and *n*-hexanol in *C. annuum and C. baccatum*, respectively.

The persisting final perceived note of cheese in *C. annuum* is dependent on *n*-isovaleric acid [21,22]. Additionally, in some chili peppers belonging to *C. baccatum*, such as the Banana pepper and Cayenna impala, dairy and blue cheese notes were found due to the presence of *n*-hexanoic acid, but they do not really affect the perceived aroma on the olfactory level.

In the peppers belonging to the *C. baccatum* species, the fruity notes are predominant, in particular the green and yellow apple typical of (*E*)-2-hexenal and pentyl isovalerate [21,22], respectively, and the perceived aroma is generally light.

3. Materials and Methods

3.1. Standard Compounds (Reagents)

A C7–C40 Saturated Alkanes (1000 µg/mL) standard mixture in hexane (49452-U) supplied by Merck Life Science (Darmstadt, Germany) was utilized for ALKANEs linear retention indices (LRIs) calculation. Forty-seven standard compounds (Table S3 from Supplementary Materials) supplied by Merck Life Science (Darmstadt, Germany) were used for the training of the panelist for sensory analysis.

3.2. SPME Extraction Conditions

For the method optimization, two SPME fibers supplied by Merck Life Science (Darmstadt, Germany) were tested: carboxen/polydimethylsiloxane (CAR/PDMS), 75 µm 1 cm long (57343-U), and divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS), 50/30 µm 1 cm long (57329-U). The fibers were conditioned before the initial use according to manufacturer's instructions, and a cleaning step of 20 min at 10 °C below fiber recommended maximum temperature was applied between consecutive analyses. GC analyses were carried out using for each test a 10 mL vial with 0.2, 0.3, and 0.4 g of ground sample, respectively, inserting the fiber 2 cm above the sample, and the best results were obtained for a 0.2 g sample weight.

Four different fiber exposure times were tested: 30, 40, 50, and 60 min. The highest volatile extraction yield was achieved after an exposure time of 50 min, and most of the

heavier molecular weight volatiles remained substantially stable thereafter. Furthermore, a sample conditioning time of 5 and 10 min was evaluated at the same temperature (30 °C, 40 °C, 50 °C, or 60 °C) employed for the extraction stage, and the analytical repeatability was excellent in both conditions. Different stirring rates (200 and 300 rpm) for sample conditioning and extraction were also investigated.

In this investigation, the (DVB/CAR/PDMS) 50/30 µm fiber was found to be the most useful in covering the wide range of chili pepper volatile analytes; a conditioning time of 5 min and an extraction temperature of 50 °C were the best compromise between equilibration time and method sensitivity. Furthermore, a time of 50 min at the same temperature and stirring rate of 300 rpm were proven to be the best choices for an exhaustive extraction of the volatiles components (Figures S6–S10 from Supplementary Materials show method optimization).

The same extraction condition was adopted for the flavored extra virgin olive oils, using 1 mL as sample volume.

After the extraction, the analytes were manually injected in splitless mode and thermally desorbed for 1 min at 260 °C in the GC injector port.

3.3. GC–MS and GC-FID Analysis

GC-MS and GC-FID analyses were carried out for qualitative and quantitative purposes, respectively.

GC-MS analyses were carried out on a GC-QP2020 system (Shimadzu, Kyoto, Japan). For the separation, an SLB-5 ms fused-silica capillary column (30 m × 0.25 mm i.d. × 0.25 µm df) (29804-U) (Merck KGaA, Darmstadt, Germany) was applied. Helium was used as carrier gas at a constant linear velocity of 30.0 cm/s, which corresponded to an inlet pressure of 24.2 kPa. An inlet liner, direct SPME type, straight design unpacked (2633501) (Merck KGaA, Darmstadt, Germany) was used. The injector was equipped with a Thermogreen LB-2 Septa, plug (20608) (Merck KGaA, Darmstadt, Germany), and the temperature was set at 260 °C. The temperature program was the following: 40 °C, held for 1 min, to 350 °C at 3 °C/min, held for 5 min. The interface and ion source temperatures were 250 °C and 200 °C, respectively. The acquisition was made in full scan mode in the mass range of 40–500 m/z, with a scanning rate interval of 0.2 s. Data handling was supported by GCMS solution ver. 4.30 software (Shimadzu, Kyoto, Japan). For the characterization, the following databases were used: W11N17 (Wiley11-Nist17, Wiley, Hoboken, NJ, USA; and FFNSC 4.0 (Shimadzu, Kyoto, Japan). The identification was performed applying two filters, namely, spectral similarity match over 85% and linear retention index (LRI) match calculated using a C7–C40 saturated *n*-alkane homolog series with a filter window of ±10 LRI units.

The LRIs were calculated applying the equation proposed by H. Van den Dool and D. J. Kratz (Equation (1)) [23], developed for programmed-temperature retention index calculation.

$$LRI = 100 \times \left[z + (t_{Ri} - t_{Rz}) / \left(t_{R(Z+1)} - t_{Rz} \right) \right] \quad (1)$$

GC-FID analyses were carried out on a GC2010 system (Shimadzu, Kyoto, Japan). Column, oven temperature program, and injection parameters were the same as for MS applications. Helium was used as carrier gas at a constant linear velocity of 30.0 cm/s, which corresponded to an inlet pressure of 97.4 kPa. The FID temperature was set at 280 °C (sampling rate 200 ms), and hydrogen and air flows were 40 mL/min and 400 mL/min, respectively. Data were collected by LabSolution software ver. 5.92 (Shimadzu, Kyoto, Japan). Quantitative results were determined as peak area percentage without any correction. Samples were analyzed in triplicates.

3.4. Statistical Procedure

Principal components analysis (PCA) bidimensional visualization, as implemented in ClustVis large version 2.0 (https://biit.cs.ut.ee/clustvis_large, accessed on 25 March 2022), was used for showing relationships between compounds classes and metabolites with

Capsicum chili peppers species, respectively. For these analyses, the compounds classes and metabolite datasets were ln (x + 1) transformed and mean-centered. Pareto scaling was used as a measure for compounds' classes–species and metabolite–species correlation and for hierarchical clustering analysis (HCA).

3.5. Sensorial Evaluation Procedure

Sensory analysis was carried out by a panel of 7 analysts trained to distinguish and describe the aroma characteristics of 47 pure standards (Table S3 from Supplementary Materials). The first step was to carry out a screening of all the chili pepper samples to identify the descriptors. The overall aroma of accessions was defined by about 61 descriptors, divided into 4 macro-areas: fresh fruity and floral notes; fresh vegetable notes; dry vegetable notes; and other notes (miscellaneous), including woody, dairy, spicy, and notes not attributable to the other categories. Figure S11 from Supplementary Materials reports a list of the descriptors identified by the panel test.

For the sensorial analysis, the peppers were chopped one at a time with an immersion blender to reduce them into pieces of 2/3 mm, and the mixture was then placed on a sheet of absorbent paper to drain the moisture. Each panel smelled the preparation for about 30 min in order to identify the top, the middle, and the bottom notes.

The intensity of the previously identified descriptor was judged on a 10-point scale from 1 = weak to 10 = very strong. The radar graphs for each sample were constructed with the positive average values, excluding the values equal to zero, the minimums, and maxima.

4. Conclusions

In this paper, the volatile fingerprinting of 17 varieties of chili peppers belonging to *Capsicum chinense*, *Capsicum annuum*, and *Capsicum baccatum* were profiled using an HS-SPME extraction method followed by GC analysis. Previously, *Capsicum baccatum's* volatile profile was not well investigated. Furthermore, this is the first work in which such a large number of chili peppers belonging to *Capsicum chinense* is analyzed and discussed in detail.

The diversity in aroma found among the studied cultivar, due to qualitative and quantitative differences of the odor-contributing volatiles, was also confirmed by the sniffing test. In particular, the sensory results revealed *C. chinense* chili peppers have fruity/exotic aromas and are characterized by a high contribution of several esters. The aroma found among *C. annuum* is due to different combinations of fruity/exotic and green/vegetable notes. The notes perceived in *Capsicum baccatum* peppers are principally fruity, and their intensity is weak in respect to that of the other pepper species.

Principal components analysis and hierarchical cluster analysis performed using percentage area of the 118 most abundant volatile compounds enabled a model to be built to distinguish between the different *Capsicum* species investigated. In addition, the volatile profile of chili extra virgin olive oil was investigated in order to find a valuable approach providing useful and comprehensive insights to evaluate the impact of chili flavor addition on extra virgin olive oil's volatile composition, which highlights the use of this approach for evaluating food traceability and authenticity.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/molecules27072355/s1, Figure S1: Hierarchical cluster analysis based on the relative percentage areas of identified compound classes; Figure S2: Hierarchical cluster analysis based on the relative percentage areas of the 118 most abundant identified volatiles; Figure S3: Aroma profile of the *Capsicum chinense* pepper from descriptive sensory analysis on the line scale (n = 10); Figure S4: Aroma profile of the *Capsicum annuum* pepper from descriptive sensory analysis on the line scale (n = 10); Figure S5: Aroma profile of the *Capsicum baccatum* pepper from descriptive sensory analysis on the line scale (n = 10); Figure S6: Influence of temperature on SPME method extraction optimization; Figure S7: Influence of time on SPME method extraction optimization; Figure S8: Influence of stirring rate on SPME method extraction optimization; Figure S9: Influence of sample

time conditioning on SPME method extraction optimization; Figure S10: Influence of sample volume on SPME method extraction optimization; Figure S11: List of descriptors used in the sensory analysis of chili peppers; Table S1: Less abundant volatile compounds contained in the chili peppers samples analyzed, expressed in area % as a GC-FID measurement; Table S2: Volatile compounds contained in the chili-pepper-flavored olive oil samples analyzed, expressed in area % as a GC-FID measurement result; Table S3: Standard key compounds used for the training of panelists for sensorial analysis; Table S4. Contribution of the variables on PC1 and PC2.

Author Contributions: Conceptualization, E.T.; methodology, D.C. and E.T.; formal analysis, F.V.; investigation, E.T. and F.V.; data curation, E.T.; writing—original draft preparation, E.T.; writing—review and editing, E.T.; supervision, L.M. and P.D. All authors have read and agreed to the published version of the manuscript.

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Sample Availability: Samples from the compounds are not available from the authors upon request.

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Supplementary material

Elucidation of analytical–compositional fingerprinting of three different species of chili pepper by using Headspace Solid-Phase Microextraction coupled with Gas chromatography–Mass spectrometry analysis, and sensory profile evaluation

Emanuela Trovato [1,*], Federica Vento [2], Donato Creti [3], Paola Dugo [1,2] and Luigi Mondello [1,2,4] **Table S1.** Less abundant volatile compounds contained in the chili peppers samples analyzed, expressed in area% as GC-FID measurement results.

	Compound	LRL_{ex}	LRL_{lib}	*Capsicum Chinense*									*Capsicum Annum*					*Capsicum Baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
15	Tiglic aldehyde	742	738	tr	tr	tr	tr	tr	tr	0.2							tr		0.06	
26	Butanoic acid	791	818		tr		tr	tr		0.17			tr							
32	5-Methyl-3-hexanone	832	842		tr	tr	tr	tr	tr	tr		0.09						tr	tr	tr
34	(*Z*)-2-Hexenal	842	842	tr										0.25	0.14	0.17	0.39	0.42	0.34	0.16
36	Ethyl iso-valerate	850	850		tr	0.17	0.16	tr	0.1			0.24								0.08
45	5-Methyl-3-hexen-2-one	897	894	tr		tr		tr	tr		0.09		0.15	tr	0.13	0.08	tr	tr	tr	tr
46	*n*-Heptanal	902	906	tr	tr	tr	tr	tr	tr		tr	0.14	0.07	tr	0.07	0.06	tr	tr	tr	0.15
47	3-(Methylthio)propionaldehyde	907	909	tr	tr	tr	tr	tr	tr	0.06	0.1	0.14	tr	tr	0.09	0.11	tr	tr	0.05	tr
48	Sorbaldehyde	914	923	tr		tr	tr		tr	tr	0.33	0.44	tr	0.08		0.3	tr	0.36	0.24	0.22
49	Sorbic aldehyde	916	914								0.19	0.48	tr	0.11		0.11	0.46	0.15	0.47	
50	γ-Butyrolactone	918	910	tr	tr	tr		tr		tr		0.18	0.08	0.24		0.12	0.13			0.35
51	3-Methyl-apopinene	921	927				tr		tr			0.07	tr	0.19	0.07		0.38	0.15		0.19
52	Ethyl tiglate	823	933		tr				tr		tr		0.06	tr	tr	tr		tr		0.09
53	α-Thujene	925	927		tr		tr	tr	tr				0.07	0.08	0.09	tr	tr	tr		
54	α-Pinene	931	933				tr					0.13	tr	tr	tr	tr		tr		tr
55	Hexyl formate	936	929				tr			tr	tr	0.06	tr	tr	0.06	0.05	tr	tr		tr
56	4-Methyl-1-hexanol	946	953	tr	tr	tr	tr	tr	tr	tr	tr	0.15	0.05	0.05	0.12	0.05	tr	tr	0.07	tr
57	3-Methyl-cyclohexanone	950	951				tr		tr	0.11	tr	0.08	0.05	tr	tr	tr		tr		tr
58	(*E*)-2-Heptenal	959	956		tr	tr	tr	tr				0.14		tr	tr	0.06	tr	0.06	0.07	0.27

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59	Isobutyl butanoate	961	953		tr	tr	tr	tr		0.46	0.06		tr	tr	0.08	0.05	tr	0.09		0.42
61	Ethyl isohexanoate	963	969	0.1	tr	0.2	tr	tr	0.17	0.26	0.05	0.27	0.05	tr	0.12	0.08	tr	0.08	0.05	0.06
62	Benzaldehyde	966	960	tr	tr		tr	tr	tr		tr	0.14	0.06	0.09	0.18	tr	0.09	0.06	tr	tr
63	Isohexanoic acid	968	986	tr	0.07		tr	tr		0.29	0.08		0.08	tr	0.08	tr	tr	0.06	0.06	
64	*n*-Heptanol	970	970	tr	0.15	tr	tr	0.16		tr		0.09	tr	tr		tr		tr	tr	0.07
65	Sabinene	972	972	tr		tr					0.06	0.18		tr	0.1		tr	tr	0.1	tr
66	β-Pinene	975	978			tr					tr	0.37	tr	tr	0.08			tr		tr
67	2-Ethylbutyl acetate	976	972	tr		tr	tr			tr	0.09				0.44	0.16	tr	tr		0.14
68	3-Methylmercapto-1-propanol	985	982	tr			tr		0.05					0.06	0.39	0.36				
72	Isobutyl 2-methylbutanoate	1001	1002	tr	tr	tr	tr	tr	0.05	tr	tr	0.18	0.07		0.11	tr		tr	0.07	tr
73	*n*-Octanal	1002	1006	tr		tr	tr	tr	tr	tr	tr	0.21	tr	tr	0.38	0.06	tr	tr	0.05	tr
74	*p*-Mentha-1(7),8-diene	1003	1004	tr	tr	tr	tr	tr		tr	tr			tr			tr	0.05	0.07	0.33

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	Compound	LRL$_{ex}$	LRL$_{lib}$	*Capsicum Chinense*									*Capsicum Annum*					*Capsicum Baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
75	Isobutyl isovalerate	1005	1005	0.06	tr	0.07	tr	tr	0.18	0.14	tr			0.06		0.15		0.13	tr	0.22
76	Ethyl (*Z*)-hex-3-enoate	1006	1003		tr	tr	tr	0	tr		tr	0.14		tr		0.06	0.08		tr	0.43
77	Isopentyl- isobutanoate	1011	1014		tr	tr	tr	tr	tr	tr	tr	0.1	tr	0.05	tr	tr			tr	
78	Pentyl 2-methylpropanoate	1014	1016	tr	tr	tr	tr	0.23	tr	0.12	tr	0.17		tr		tr	0.08	tr	0.09	0.15
79	(*E*)-6-Methylhept-4-en-1-ol	1020	1019	0.08	tr	0.23	0.13		tr	0.29		0.06	tr	tr	0.15	0.06	0.05	tr	0.09	tr
82	2-Ethyl-1-hexanol	1029	1031	tr	0.05		tr	tr	tr	tr	0.07		0.1	0.21	0.44	0.43	tr	0.09	0.1	0.26
83	3-Methyl-1-heptanol	1034	1041	tr	tr	tr	tr	tr			0.16	0.24					tr	tr	tr	tr
85	Benzyl alcohol	1036	1040	tr		tr	tr	tr	tr	tr	0.1	0.14	tr	0.1	0.11	0.15	tr	tr	0.1	tr
86	9-Methyl-1-decene	1038	1041	tr	tr	tr	tr		tr	tr	tr	0.32	0.06	0.05		0.22	tr	0.14	0.13	tr
87	Phenylacetaldehyde	1043	1045	0.12	tr	tr	tr	tr	tr	0.05	0.07	0.14	0.07	0.16	0.17	0.19	0.28	tr	0.06	0.19
88	5-Methyldecane	1044	1054					tr	tr		tr				0.17	tr	0.09		0.27	
89	Amyl pivalate	1045	1047	tr		tr	0.1	0.07	0.06		tr		0.06	0.34				0.06		
92	2-Methyloctanal	1052	1059	tr	tr	tr			tr	0.11	tr	0.14	0.22	tr	0.06	tr	tr	0.28	tr	0.05
93	γ-Terpinene	1055	1058	tr			tr	tr	tr	tr	0.19	0.18	0.18	0.06	0.17	0.06	tr	0.19		0.4
95	*n*-Octanol	1071	1076	tr	tr	tr	tr	0.11	tr	0.12		0.08	tr	0.05	0.23	0.16	tr	tr	0.06	tr
96	(*E*)-3-Octen-1ol	1074	1081	tr	tr	tr	tr			tr	tr	0.13	0.06	tr	0.22	0.05	tr	0.05	0.06	0.13
97	*n*-Heptanoic acid	1080	1116	tr	tr	tr	0.07		tr	tr		0.1	tr	0.05	0.12	0.05	0.1	0.16	0.12	0.06
102	2-Methylbutyl 2-methylbutanoate	1101	1104	tr	tr	tr	tr	tr	0.07	tr	tr			tr		tr	tr	0.26	tr	0.11
108	Phenethyl alcohol	1113	1113	0.06		tr	tr	tr	tr	tr	tr	0.16	tr	tr	tr	tr	tr	tr	0.3	tr
109	*p*-Menta-1,3,8-triene	1122	1112	tr		tr				tr	tr	tr		tr	tr	tr	tr	tr		0.42
110	2-Ethylhexoic acid	1127	1137	tr		0.19			0.13	tr	tr	0.07		tr	tr	tr	tr	0.12		0.28
113	Pentyl 2-methylbutanoate	1136	1142	tr	tr	tr	0.19	tr	0.29	tr	0.19	0.15	0.08	tr	0.36	0.11	0.07		0.21	tr
115	(*Z*)-3-Hexenyl isobutanoate	1141	1146	tr	0.06	tr	0.1		0.1	0.11	tr	0.1				0.09		tr		
118	3-Methylbut-2-enyl 3-methylbutanoate	1148	1150	tr		0.1	tr	0.06	0.16		tr	0.06			tr	tr				
119	Dictyopteren D'	1150		0.21	0.16	0.1	0.22		0.16		tr	0.08			0.09	tr	0.29			
120	neo-Isopulegol	1152	1148	tr	0.1	0.05	tr	tr	tr	0.07	tr	0.18	0.21	0.05	0.09	0.05	tr	0.05	0.06	0.08
121	(*E*)-Pinocamphone	1160	1160	tr	tr	tr	tr			tr	tr	0.15	tr	0.06	0.1	0.11	tr	tr		0.36
122	Tetrahydrolavandulol	1168	1162			tr		tr	tr	0.22		0.28	tr	tr	0.11	0.13	0.05	tr	0.05	
123	Ethyl benzoate	1170	1170	tr	tr	tr	tr	tr		tr	tr	0.23		tr	0.13	tr		tr		0.22
124	Benzenecarboxylic acid	1175	1213	tr	tr	tr	tr			tr		0.1	0.1	tr						tr

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	Compound	LRL$_{ex}$	LRL$_{lib}$	*Capsicum Chinense*									*Capsicum Annum*					*Capsicum Baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
126	Neoisomenthol	1182	1189	tr			tr		0.1				tr							0.1
127	Terpinen-4-ol	1183	1184					tr		tr		0.32								
128	Nonanol	1185	1176	tr	tr	0.12	0.28	tr	0.24	tr	tr	0.12		tr					0.06	
129	*n*-Octanoic acid	1188	1192	0.07	tr	tr	tr	tr	tr	tr		0.06	tr	tr	0.12	0.09			tr	0.06
130	Ethyl (4*Z*)-4-octenoate	1191	1184	tr			tr	tr	tr	0.06	tr				0.06	tr	tr	tr		tr
131	Hexyl butanoate	1192	1195	tr	tr	tr			0.07	tr	tr	0.07	tr		0.1	0.06	tr	tr	tr	tr
132	Methyl salicylate	1193	1192	tr	tr	tr	0.05	tr		tr	0.11	0.33	tr	0.29	0.12	tr	tr	0.05	0.07	tr
133	*n*-Dodecane	1196	1187		tr	tr							tr	tr	0.12	0.07	tr	tr	0.05	0.15
136	Pelargol	1208	1200	tr			tr	tr	tr	tr	tr	0.23	tr	0.06	0.07	0.13		tr	tr	tr
137	4-Methylhexyl isobutanoate	1215	1220	0.09	0.05	tr	0.32	tr	tr	tr	tr	0.08		tr	0.08	0.06	tr	tr	0.06	
139	ESTER	1226		0.4	0.29	0.34	0.1	0.14	0.18	0.17	0.4	0.11	0.06	tr	0.09	0.05	0.06	tr	tr	tr
146	ESTER	1257		0.06	0.05	tr	tr	tr	tr	tr	tr			tr	0.14	0.07	tr	tr	tr	tr
147	2-Methyldodecane	1263	1265	tr	tr	tr	0.07	tr	0.1	tr	tr	0.1	tr	tr	0.17	tr	0.06	tr	0.05	tr
148	Ethyl salicylate	1273	1270	0.18	tr	0.13	tr	tr	0.12	0.09	0.05	0.18	tr	tr	0.08	0.05	tr	tr	0.07	0.37
149	*n*-Nonanoic acid	1275	1289	0.09	tr	0.08	0.13	0.11	0.08	tr	0.09	0.14	0.06	tr	0.19	0.06		tr	tr	tr
150	Hexyl angelate	1285	1283	0.19	tr	tr	0.26		tr	tr	tr	0.07	tr	tr	0.18	tr	tr	tr	tr	tr
153	5-Methylhexyl 2-methylbutanoate	1294	1299	tr	0.08	tr	0.23	tr	tr	tr				tr		0.1	tr			
154	*n*-Tridecane	1298	1300	0.06	tr	tr	0.08		tr	tr	tr	0.2	tr	0.14	0.19		0.1	tr	0.06	0.09
156	Hexyl pentanoate	1301	1293		0.12		0.11	0.29							0.1	tr				
161	Dihydro citronellol acetate	1316	1319		tr	tr	tr	0.07		tr		0.1	tr	tr	tr	tr	tr	tr	tr	0.09
162	(E)-3-Hexenyl tiglate	1317	1319	0.09	0.19	0.08	0.1	tr	tr	tr	tr	0.19		tr		tr	tr	tr	0.06	tr
163	(Z)-3-Hexenyl tiglate	1321	1325	0.11	0.07	0.06	tr	0.07	0.11	tr	0.25	0.1	tr	tr	0.09	tr	tr			tr
164	Hexyl tiglate	1328	1329	0.06	0.16	0.07	0.07	0.26	0.1	tr	tr	0.08				tr	tr			tr
166	1-Nonadecyne	1334		0.05			0.16		0.07	tr		0.18				tr			tr	
168	Octyl isobutanoate	1342	1346	tr	tr	0.08	0.18	0.11	tr			0.06				tr		tr	tr	
169	(Z)-Hept-3-enyl 2-methylbutanoate	1345		0.09	0.28	0.09	0.05	0.08	0.1	0.06		0.07			0.11	tr				
173	Ethyl 8-methylnonanoate	1358	1359	0.15	0.2	0.18	0.28	0.05	tr	0.06	tr	0.07		tr	0.06	tr	0.1		tr	tr
175	*n*-Decanoic acid	1374	1398	tr	tr	0.33	tr	tr	tr	tr	tr			tr	0.09		tr		tr	tr
184	Benzyl isovalerate	1395	1399		0.14		0.15	tr	0.06	tr	tr									
185	*n*-Tetradecane	1397	1400	tr		tr			0.09	tr	0.06	0.24	0.05	0.05	0.23	0.1	tr	tr	0.08	0.06
187	*n*-Dodecanal	1409	1412	tr	0.06	tr	tr	tr	tr	tr	tr	0.06	tr	tr	0.13	0.05	tr	tr	0.07	tr

molecules
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188	(Z)-α-Bergamotene	1411	1416	tr	tr	tr	tr	tr	tr		tr	0.09		tr	0.13	0.13	tr	tr	tr	tr
189	Longifolene	1413	1412	tr	0.1	tr	tr	tr	tr	tr		0.18				tr	tr	tr	0.09	
190	α-Cedrene	1416	1414	0.12	tr	tr	0.2	0.29	tr	tr	0.09		tr			0.1	0.07			
191	(E)-Caryophyllene	1420	1424		0.1	tr	tr	tr	tr	tr	tr					tr	0.12	0.32		tr
193	γ-Elemene	1427	1432	0.09	0.26	0.12	0.12	0.16	0.08	tr		0.12					0.1			
	Compound	LRL$_{ex}$	LRL$_{lib}$	*Capsicum Chinense*									*Capsicum Annum*					*Capsicum Baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
194	β-Copaene	1431	1433	0.3	0.29	0.16	0.08	0.15	tr	tr		0.24	tr		tr		0.2		tr	
195	Octyl 2-methylbutanoate	1434	1433	0.07	0.39	0.19	0.14	0.25	0.07		tr				0.31	0.13				
201	Cadina-3,5-diene	1449	1452	tr	tr		0.07	0.12				0.1		tr	0.13					
203	(*E*)-β-Farnesene	1453	1452				tr	0.28		tr				tr	0.36	0.09	tr	tr	0.21	
204	α-Humulene	1456	1454	0.07	0.13	0.08	0.06	0.34	0.06	tr	tr			tr	0.1		tr	tr	tr	
205	α-Patchoulene	1461	1459	0.08			0.13	0.11	tr	tr			0.08		tr	tr			tr	tr
208	Cadina-1(6),4-diene	1474	1474	0.1	0.1	0.09	0.13	0.07	0.12	tr	tr	0.2				tr	tr		0.1	tr
209	γ-Muurolene	1475	1478	0.16	0.27	0.08	0.2	0.1	0.11	tr	tr	0.32		tr	tr		tr	tr	0.28	tr
215	6-Methylhept-4-en-1-yl 2-methylpentanoate	1493	1484	0.14	0.22	0.25	0.13	0.24	tr	tr		tr		0.07	tr	tr	0.1	tr	0.27	0.05
216	γ-Amorphene	1494	1490	0.18	0.15	0.08	0.12	0.08	tr	tr		0.09					tr		0.07	
221	ESTER	1512		tr	tr	0.08	tr	tr	tr						0.1	tr	tr			tr
222	γ-Cadinene	1514	1512	0.16	0.14	0.05	0.11	0.08	tr	tr					0.08	tr		tr	tr	tr
224	(*E*)-Calamenene	1522	1527	0.36	0.2	0.22	0.36	0.16	0.16	tr	tr	0.13			0.08	0.06		tr	0.09	tr
225	Citronellyl butanoate	1533	1529	0.09	0.06	0.1	0.06	0.05	0.07	tr		0.07				tr	tr			tr
226	(*E*)-Cadina-1,4-diene	1534	1536	tr		0.09	tr	0.08	tr		tr	0.11		tr	0.15	tr	0.16		tr	tr
228	ESTER	1546		0.13	0.14	0.16	0.06	0.06	tr	tr	tr	0.08			0.09	tr	tr			tr
229	Dodecanethiol	1547	1543	tr	tr	0.08	0.09	tr	tr	tr	tr	0.07		tr	0.16	tr	tr			
230	Geranyl butanoate	1551	1559	0.06	0.17	tr	0.07	0.2								tr				
231	(*E*)-Nerolidol	1558	1561			tr											0.4			
232	12-Methyl-oxa-cyclododecan-2-one	1559		0.06			0.12	tr							0.06	tr				
233	2-Methyl pentadecane	1561	1567	0.44	0.18	0.14	0.19	0.06	tr	tr	tr	0.17		0.1	0.12	tr	tr	tr	tr	tr
234	3-Methyl pentadecane	1568	1574	0.08	0.05	tr	tr	tr	tr	tr	tr	0.08		tr	0.12	tr	tr	tr		tr
236	(*Z*)-2-Tridecen-1-ol	1578	1572	tr	tr	0.13	tr	0.06	tr				tr							tr
239	Ethyl dodecanoate	1591	1598	0.19	0.12		0.14	0.08	0.07				tr		0.07	tr	tr			tr

240	*n*-Hexadecane	1598	1600	tr	0.05	0.06	tr	tr	0.07	tr	tr	0.15		0.06	0.11	tr	0.07	tr		tr
241	8-Methylnonanoic acid, 2-methylbutyl ester	1606	1610	0.42	0.35	0.2	0.16	0.08	tr	tr						0.07	0.21			
242	α-Corocalene	1543	1544	tr	tr	tr	tr	tr	tr		tr				0.11	tr				
243	Isopentyl 8-methylnon-6-enoate	1594	1592	tr	tr	0.14	tr	tr	tr	tr						tr	tr			tr
244	Oxacyclotetradecan-2-one	1629	1632	0.08	0.25	0.36	0.35	tr	tr	tr		0.15			0.15	0.06	0.21		tr	
245	14-Methyl-oxacyclotetradecan-2-one	1650	1660	0.15	0.05	0.12	0.27	tr		tr	tr				0.12	tr	0.4			tr
	Compound	LRL$_{ex}$	LRL$_{lib}$	*Capsicum Chinense*									*Capsicum Annum*					*Capsicum Baccatum*		
				1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**	**16**	**17**
246	Cadin-4-en-10-ol	1657	1659	0.11	tr		tr	0.12	tr	tr					0.17	tr		tr		tr
247	2-Methyl hexadecane	1660	1664	0.32	0.11	0.15	0.08	tr	tr	tr		0.16			0.23	tr	0.23			
248	8-hydroxy-isobornyl isobutanoate	1665	1676	tr	0.06	0.08	0.06	tr	tr	tr	tr	0.12	tr	0.07	0.18	tr		tr	tr	0.05
251	*n*-Heptadecane	1696	1700	0.35	0.22	0.18	0.1	tr	0.06	tr	tr	0.2		0.07	0.1	tr	tr	tr		tr
253	Hexyl 8-methylnon-6-enoate	1720	1730	tr	tr	0.28	tr	tr	tr	tr	tr	0.11		tr	0.12	tr	tr	tr		
254	2-Methyl-heptadecane	1762	1763	tr	tr	tr	tr	tr	tr			0.05						tr		
255	(*Z*)-2-Pentadecenal	1764	1760	tr	tr	tr	tr	tr	tr						0.1					
256	3-Methyl-heptadecane	1767	1774	tr	tr	tr	tr	tr	tr	tr					0.09		tr			
257	(*Z*)-2-Pentadecenol	1778	1776	tr	tr	tr	tr	tr	tr	tr	tr	0.12	tr		0.1				tr	tr
258	1-Tetradecyl acetate	1804	1810	tr	tr	tr	tr	tr	tr	tr	tr				0.14					
259	Pentadecylic acid	1823	1869		tr	tr		0.05		tr					0.16					
260	Pentadecanolide	1830	1827	tr	tr	tr	tr	tr							0.16					tr
263	ESTER	1861		tr	tr	0.24	tr	tr	tr											
263	*n*-Hexadecanol	1884	1884	tr	tr	tr	tr	0.08	tr											
264	n-Heptadecanal	1915	1918	tr	tr	tr	tr	tr	tr	tr		0.07	tr		0.08		tr			tr
265	Hexadecanolact-16-one	1934	1938	tr	tr	tr	tr	tr	tr				tr		0.14	tr				tr
266	1-Hexadecanol acetate	2003	2009	tr	tr	tr	tr	tr				0.08					tr			
267	Octadecyl acetate	2205	2212	tr	tr	tr		tr		tr									0.07	
268	*n*-Heptacosane	2699	2700					tr										0.05		268
269	*n*-Octacosane	2798	2800					tr				0.27					tr	tr		269
	Total			**6.63**	**6.44**	**6.58**	**7.19**	**5.16**	**3.81**	**3.22**	**2.88**	**14.00**	**2.18**	**3.30**	**12.3**	**5.42**	**5.13**	**3.43**	**5.21**	**6.91**	

The compounds number is reported in order of elution, considering the total number of compounds eluted. For the identification of the compounds not reported in this table, see Table 1. tr = trace compound.

Table S2. Volatile compounds contained in the chili-pepper-flavored olive oil samples analyzed, expressed in area% as GC-FID measurement results.

	Compound	LRI_{exp}	LRI_{lib}	EVO1	EVO2	EVO3
1	(E)-2-Butenal	619	629	0.08	0.09	0.03
4	Acetic acid	659	661	1.84	1.59	1.39
9	3-Penten-2-one	690	691		1.53	
11	Acetoin	726	716	0.04		0.04
13	Isopentyl alcohol	733	729	0.03	0.04	0.05
14	sec-Butylcarbinol	738	733			0.04
19	Toluene	764	763	0.12		
24	3-Methylcrotonaldehyde	787	780	0.01		0.03
28	n-Hexanal	801	801	5.07	5.39	1.70
33	4-Methyl-1-pentanol	838	832		0.03	0.60
34	(Z)-2-Hexenal	842	842	0.27	37.41	0.21
37	(E)-2-Hexenal	850	850	30.38	2.01	19.21
41	(E)-2-Hexenol	864	864	6.33	2.39	12.64
42	n-Hexanol	868	867	4.30	2.95	3.34
44	n-Pentanoic acid	889	918	0.04		0.08
46	n-Heptanal	902	906	0.65	0.29	0.11
48	Sorbaldehyde	914	923	0.12	0.38	0.04
49	Sorbic aldehyde	916	914	0.20	0.20	0.03
53	α-Thujene	925	927			0.02
54	α-Pinene	931	933	0.05	0.01	0.02
58	(E)-2-Heptenal	959	956	1.34	0.78	0.51
62	Benzaldehyde	966	960	0.18	0.20	0.18
64	n-Heptanol	970	970	0.09		0.06
65	Sabinene	972	972	0.06	0.04	0.08
66	β-Pinene	975	978	0.13		0.14
69	6-Methyl-hept-5-en-2-one	984	986	1.12	0.30	0.18
80	p-Cymene	1025	1024	0.29	0.10	0.04
81	Limonene	1028	1030	1.82	0.46	0.22
84	(Z-β-Ocimene	1035	1035			0.13
85	Benzyl alcohol	1036	1040		0.22	0.26
90	(E)-β-Ocimene	1046	1046	1.23	0.49	1.16
94	(E)-2-Octenal	1067	1058	0.13	0.11	0.05
95	n-Octanol	1071	1076	0.09	0.08	0.02
98	Guaiacol	1086	1094	0.03	0.16	
100	3-Methylbutyl 2-methylbutyrate	1098	1104			0.18

103	n-Nonanal	1103	1107	5.30	2.11	1.46
105	2-Methylbutyl isovalerate	1106	1109			0.07
111	(4E,6Z)-Alloocimene	1128	1128	0.07	0.05	0.05
113	Pentyl 2-methylbutyrate	1136	1142			0.2
114	(E,E)-Allocimene	1140	1145	0.08		
115	(Z)-3-Hexenyl isobutyrate	1141	1146			0.32
116	Pentyl isovalerate	1142	1143			0.63
117	Hexyl isobutyrate	1146	1150		0.02	0.27
123	Ethyl benzoate	1170	1170			0.06
127	Terpinen-4-ol	1183	1184	0.03		
132	Methyl salicylate	1193	1192	0.24	0.10	0.16
133	*n*-Dodecane	1196	1200	0.03		0.04
134	4-Methylpentyl 2-methylbutanoate	1198	1202		0.42	3.85
135	4-Methylpentyl 3-methylbutanoate	1209	1206			11.12
136	Pelargol	1208	1200	1.46	1.66	
137	4-Methylhexyl isobutyrate	1215	1220			0.02
141	(Z)-3-Hexenyl 2-methylbutyrate	1233	1231		0.11	
143	Hexyl 3-methylbutyrate	1246	1243		0.05	1.97
144	(E)-Hex-2-enyl 3-methylbutanoate	1248	1243	0.03		0.29
151	6-Methylhept-4-en-1-yl isobutyrate	1289	1293			0.11
152	3-Methylpentyl (2E)-2-methyl-2-butenoate	1291	1300			0.06
153	5-Methylhexyl 2-methylbutanoate	1294	1299			0.03
155	5-Methylhexyl 3-methylbutanoate	1300	1303			0.14
159	4-Methylhexyl 2-methylbutanoate	1308	1307			0.03
160	4-Methylpentyl 4-methylpentanoate	1313	1315			0.28
163	(Z)-3-Hexenyl tiglate	1321	1325			0.03
165	Heptyl 2-methylbutyrate	1332	1333			0.04
167	Heptyl isovalerate	1338	1338			0.17
168	Octyl isobutyrate	1342	1346			0.03
170	α-Cubebene	1347	1347		0.03	0.11
177	Cyclosativene	1370	1367	0.23	0.09	0.61
178	α-Copaene	1376	1375	1.28	0.44	3.00
180	6-Methylhept-4-en-1-yl 3-methylbutanoate	1385	1388	0.01		0.48
181	β-Elemene	1389	1390	0.02		0.02
183	6-Methylheptyl 2-methylbutanoate	1394	1398			0.06
184	Benzyl isovalerate	1395	1399			0.06
185	n-Tetradecane	1397	1400	0.02	0.04	0.07
188	(Z)-α-Bergamotene	1411	1412	0.01		
191	(E)-Caryophyllene	1420	1424	0.05	0.02	
194	β-Copaene	1431	1433			0.06
196	(E)-α-Bergamotene	1435	1432		0.08	
203	(E)-β-Farnesene	1453	1452		0.01	0.01

204	α-Humulene	1456	1454			0.01
208	Cadina-1(6),4-diene	1474	1474			0.01
211	γ-Himachalene	1483	1481		0.12	0.37
223	δ-Cadinene	1519	1512	0.03	0.02	0.05
224	(E)-Calamenene	1522	1527			0.03
	Total			**64.93**	**62.62**	**69.17**

The compound's number is reported in order of elution, considering the total number of compounds identified in chili peppers.

Table S3. Standard key compounds used for the training of panelists for sensorial analysis.

	Compound	
1	Isovaleric aldehyde	590-86-3
2	2-Methylbutyraldehyde	96-17-3
3	3-Methyl-2-butanol	598-75-4
4	Acetoin	513-86-0
5	Isopentyl alcohol	123-51-3
6	Isobutyric acid	79-31-2
7	2,3-Butadienol	19132-06-0
8	Isopentyl formate	110-45-2
9	Butanoic acid	107-92-6
10	(*Z*)-3-Hexenal	6789-80-6
11	*n*-Hexanal	66-25-1
12	Ethyl 2-methylbutyrate	53956-13-1
13	(*E*)-2-Hexenal	505-57-7
14	Isovaleric acid	503-74-2
15	*n*-Hexanol	111-27-3
16	2-Methylbutyric acid	116-53-0
17	*n*-Pentanoic acid	109-52-4
18	3-(Methylthio)propionaldehyde	3268-49-3
19	4-methylpentanoic acid	646-07-1
20	3-Methylmercapto-1-propanol	505-10-2
21	*n*-Hexanoic acid	142-62-1
22	Ethyl hexanoate	123-66-0
23	Isobutyl 2-methylbutyrate	2445-67-2
24	Phenylacetaldehyde	122-78-1
25	Guaiacol	90-05-1
26	2-Methylbutyl 2-methylbutyrate	2445-78-5
27	3-methylbutyl 3-isovalerate	659-70-1
28	2-Methylbutyl isovalerate	2445-77-4
29	3-Methylpentyl isobutyrate	84254-84-2
30	Phenethyl alcohol	60-12-8
31	(*Z*)-3-Hexenyl isobutyrate	41519-23-7
32	Pentyl isovalerate	25415-62-7
33	3-Methoxy-2-isobutylpyrazine	24683-00-9
34	Methyl salicylate	119-36-8
35	4-Methylpentyl 2-methylbutanoate	35852-40-5
36	4-Methylpentyl 3-methylbutanoate	850309-45-4
37	(*Z*)-3-Hexenyl 2-methylbutyrate	53398-85-9
38	(*Z*)-3-Hexenyl 3-methylbutyrate	35154-45-1
39	Hexyl 3-methylbutyrate	10032-13-0
40	(E)-Hex-2-enyl 3-methylbutanoate	68698-59-9

41	Heptyl isobutyrate	2349-13-5
42	Ethyl salicylate	118-61-6
43	*n*-Nonanoic acid	112-05-0
44	4-Methylhexyl 2-methylbutanoate	850309-46-5
45	4-Methylpentyl 4-methylpentanoate	35852-42-7
46	*n*-Decanoic acid	334-48-5
47	(E)-Caryophyllene	87-44-5

Table S4. Contribution of the variables on PC1 and PC2.

	Compound	Without EVOOs PC1	Without EVOOs PC2	With EVOOs PC1	With EVOOs PC2
1	(E)-2-Butenal	0.000	0.034	0.000	0.045
2	3-methyl-2-Butanone	0.001	0.110	0.000	0.144
3	Isovaleric aldehyde	0.001	0.128	0.000	0.145
4	Ethanoic acid	0.024	73.790	0.121	69.630
6	2-Methylbutyraldehyde	0.007	0.288	0.003	0.296
7	3-Methyl-2-butanol	0.005	0.039	0.003	0.043
8	(Z)-2-Buten-1-ol	0.039	0.000	0.026	0.002
9	3-Pentenone	0.013	0.062	0.002	0.031
10	Propionic acid	0.008	0.027	0.005	0.034
11	Acetoin	0.174	23.219	0.269	22.832
12	Isoprenol	0.017	0.097	0.011	0.104
13	Isopentyl alcohol	0.005	0.067	0.002	0.086
14	sec-Butylcarbinol	0.001	0.158	0.002	0.163
16	Isopropyl ethyl ketone	0.003	0.002	0.002	0.003
17	Ethyl iso-butyrate	0.007	0.030	0.004	0.038
18	Isobutyric acid	0.001	0.038	0.001	0.039
19	Pentyl alcohol	0.000	0.001	0.000	0.000
20	Toluene	0.027	0.000	0.021	0.001
21	(E)-2-Penten-1-ol	0.001	0.006	0.001	0.009
25	2,3-Butadienol	0.024	0.000	0.017	0.002
27	(Z)-3-Hexenal	0.002	0.004	0.002	0.006
28	n-Hexanal	13.869	0.129	10.528	0.180
29	Ethyl lactate	0.029	0.001	0.020	0.003
30	2-Hexanol	0.127	0.001	0.089	0.009
31	4-Methyl-2-pentenal	0.199	0.000	0.142	0.001
34	Isovaleric acid	0.000	0.030	0.000	0.038
35	4-Methyl-1-pentanol	0.472	1.281	0.460	0.358
36	(Z)-2-Hexenal	0.007	0.000	0.782	5.406
37	Ethyl 2-methylbutyrate	0.007	0.006	0.007	0.001
38	(E)-2-Hexenal	83.586	0.162	85.784	0.226
40	(E)-3-Hexenol	0.080	0.027	0.045	0.000
41	(Z)-3-Hexenol	0.008	0.010	0.008	0.003
42	(E)-2-Hexenol	0.213	0.170	0.596	0.000

43	n-Hexanol	0.734	0.009	0.743	0.058
58	(E)-2-Heptenal	0.000	0.000	0.003	0.007
68	6-Methyl-hept-5-en-2-one	0.000	0.015	0.002	0.008
81	Limonene	0.000	0.002	0.003	0.000
90	(E)-β-Ocimene	0.288	0.013	0.247	0.010
91	Isopentyl butyrate	0.000	0.009	0.000	0.010
99	Isobutyl tiglate	0.001	0.008	0.000	0.009
103	n-Nonanal	0.000	0.014	0.033	0.014
106	3-Methylpentyl isobutyrate	0.007	0.001	0.007	0.000
114	(E,E)-Allocimene	0.005	0.001	0.004	0.000
116	Pentyl isovalerate	0.007	0.009	0.005	0.007

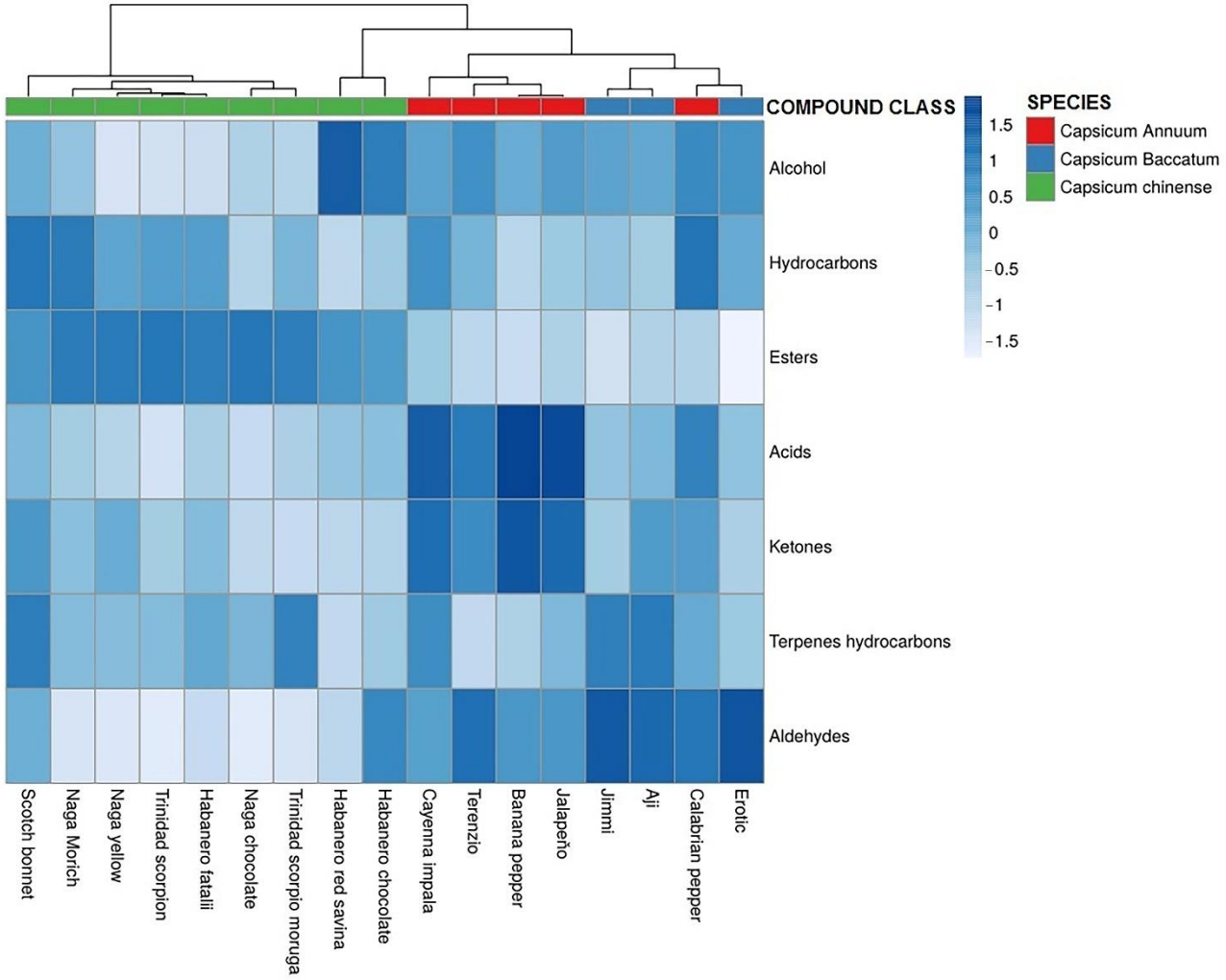

Figure S1. Hierarchical cluster analysis based on relative percentage areas of identified compounds classes. Original values are ln(x + 1)-transformed. Rows are centered; Pareto scaling is applied to rows. Imputation is used for missing value estimation. Columns are clustered using correlation distance and average linkage. There is a total of 7 rows and 17 columns.

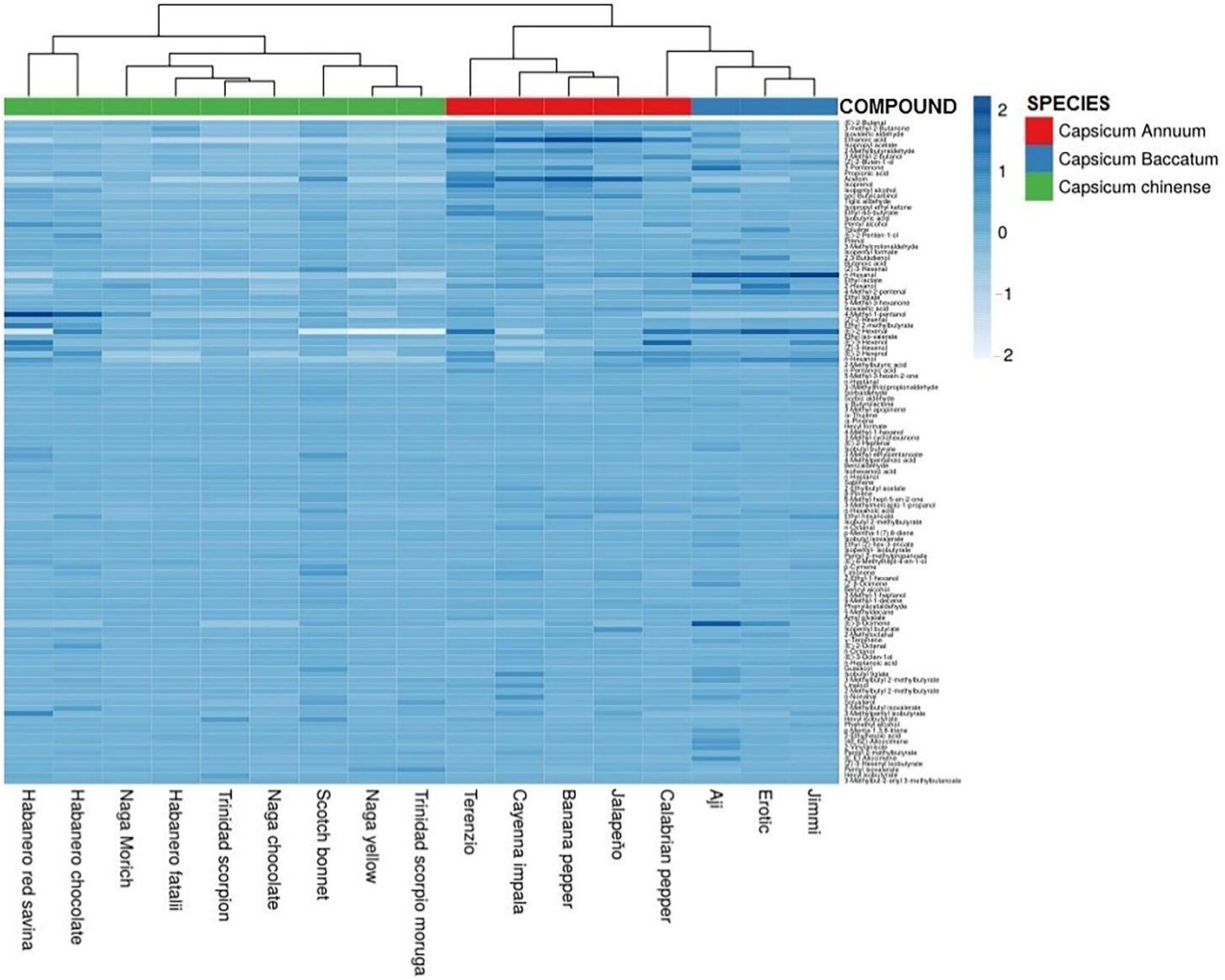

Figure S2. Hierarchical cluster analysis based on relative percentage areas of the 118 most abundant identified volatiles. Original values are ln(x + 1)-transformed. Rows are centered; Pareto scaling is applied to rows. Imputation is used for missing value estimation. Columns are clustered using correlation distance and average linkage. There is a total of 118 rows and 17 columns.

Capsicum chinense

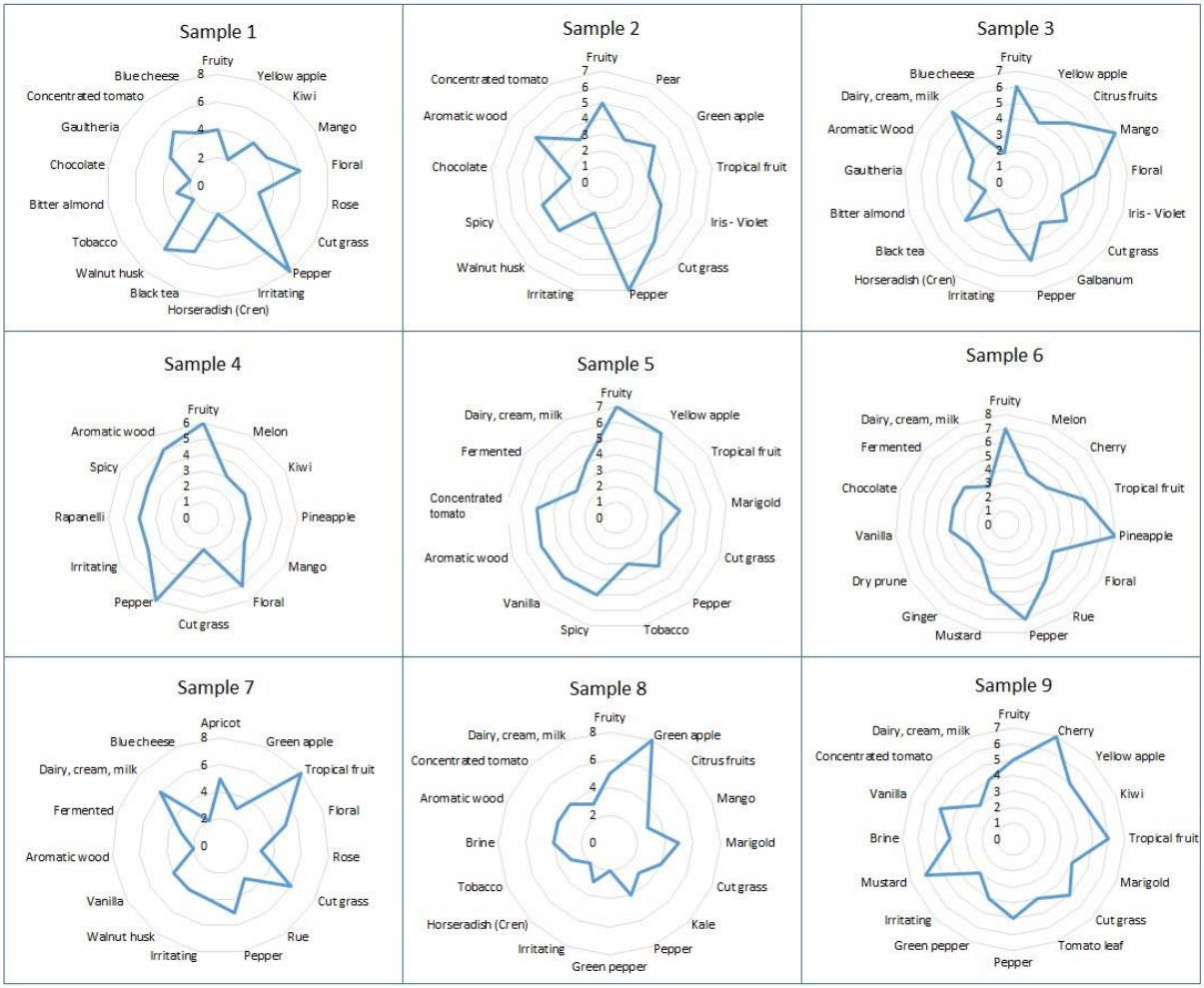

Figure S3. Aroma profile of the *Capsicum chinense* pepper from descriptive sensory analysis on line scale (n = 10). Sample 1 (Naga Morich), sample 2 (Trinidad Scorpion), sample 3 (Habanero Fatalii), sample 4 (Naga Yellow), sample 5 (Naga Chocolate), sample 6 (Trinidad Scorpio Moruga), sample 7 (Habanero Red Savina), sample 8 (Habanero Chocolate), and sample 9 (Scotch Bonnet).

Capsicum annuum

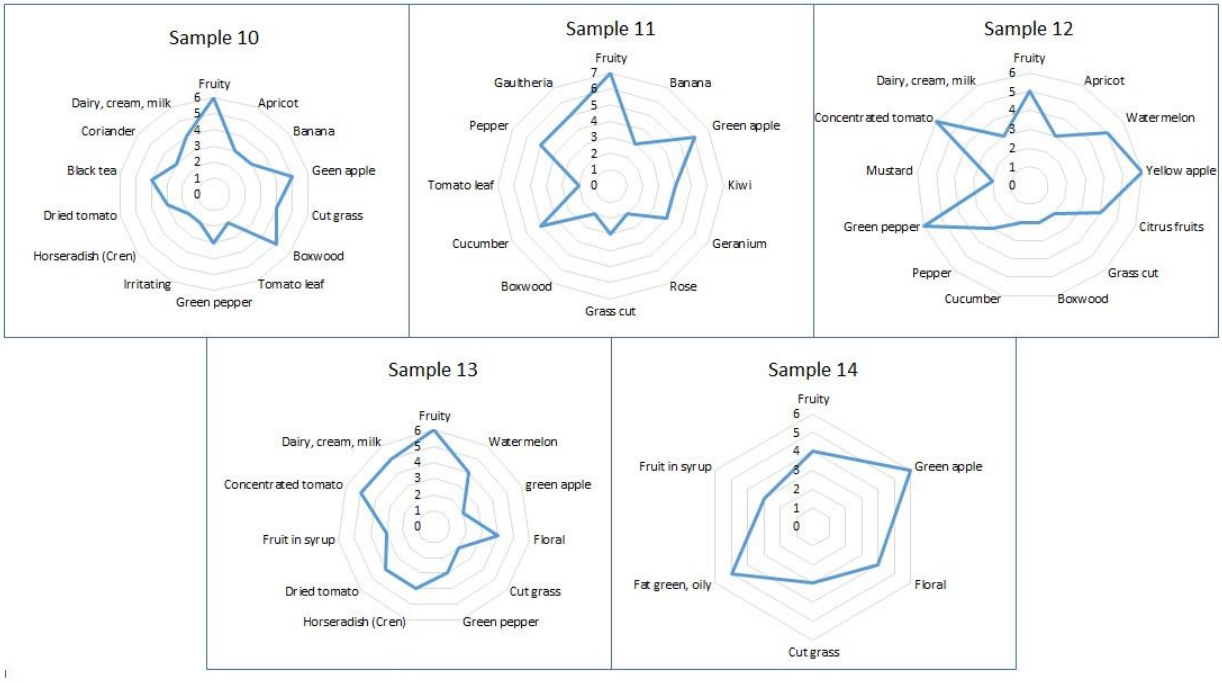

Figure S4. Aroma profile of the *Capsicum annuum* pepper from descriptive sensory analysis on line scale (n = 10). Sample 10 (Banana Pepper), sample 11 (Terenzio), sample 12 (Cayenna Impala), sample 13 (Jalapeňo), and sample 14 (Calabrian pepper).

Capsicum baccatum

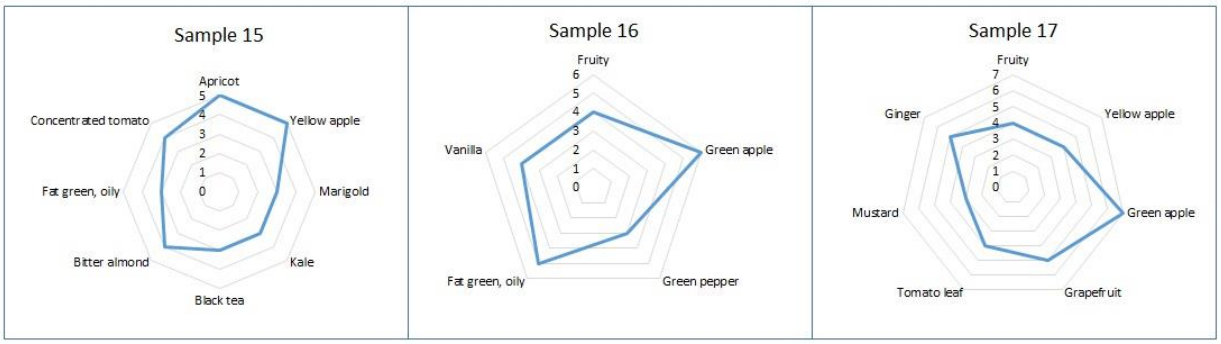

Figure S5. Aroma profile of the *Capsicum baccatum* pepper from descriptive sensory analysis on line scale (n = 10). Sample 15 (Erotic), sample 16 (Jimmi), and sample 17 (Aji limòn).

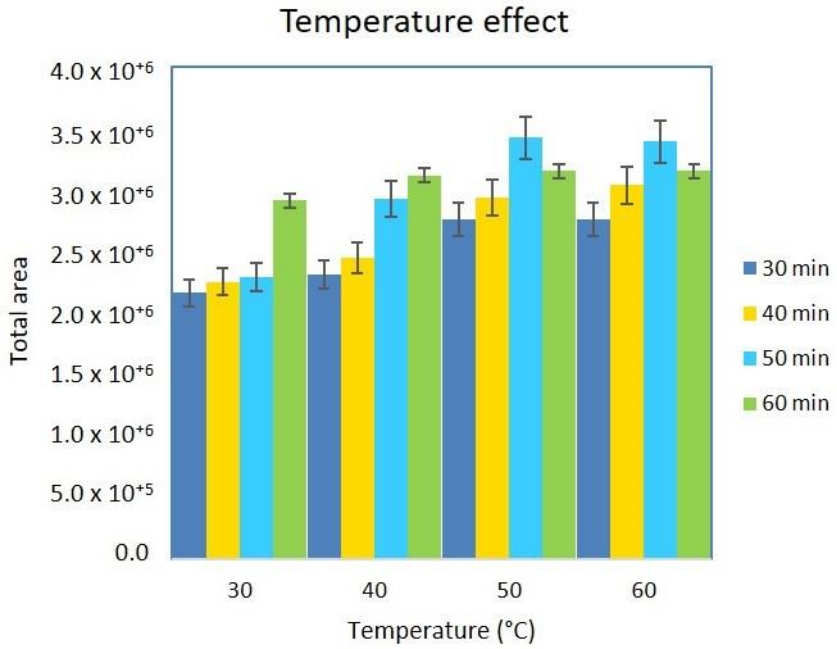

Figure S6. Influence of temperature on SPME method extraction optimization.

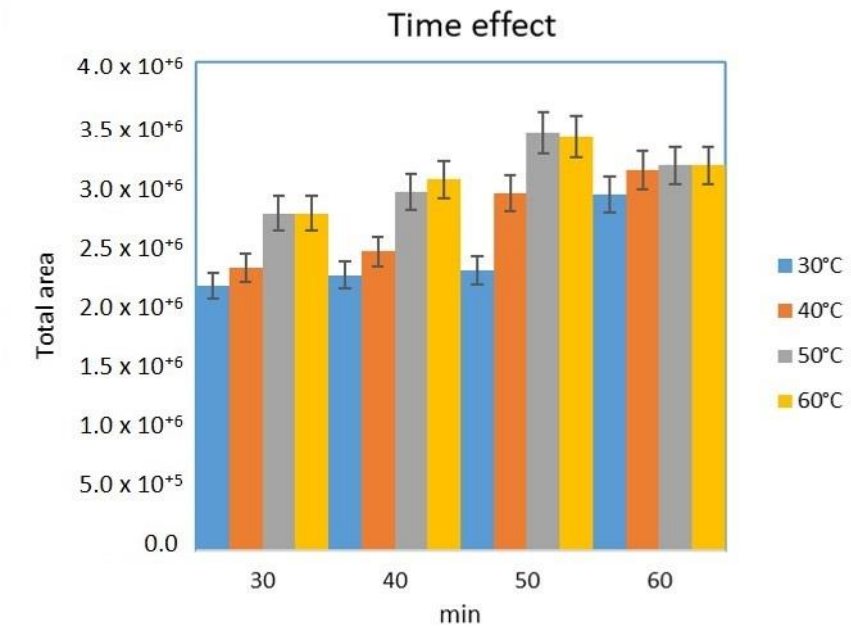

Figure S7. Influence of time on SPME method extraction optimization.

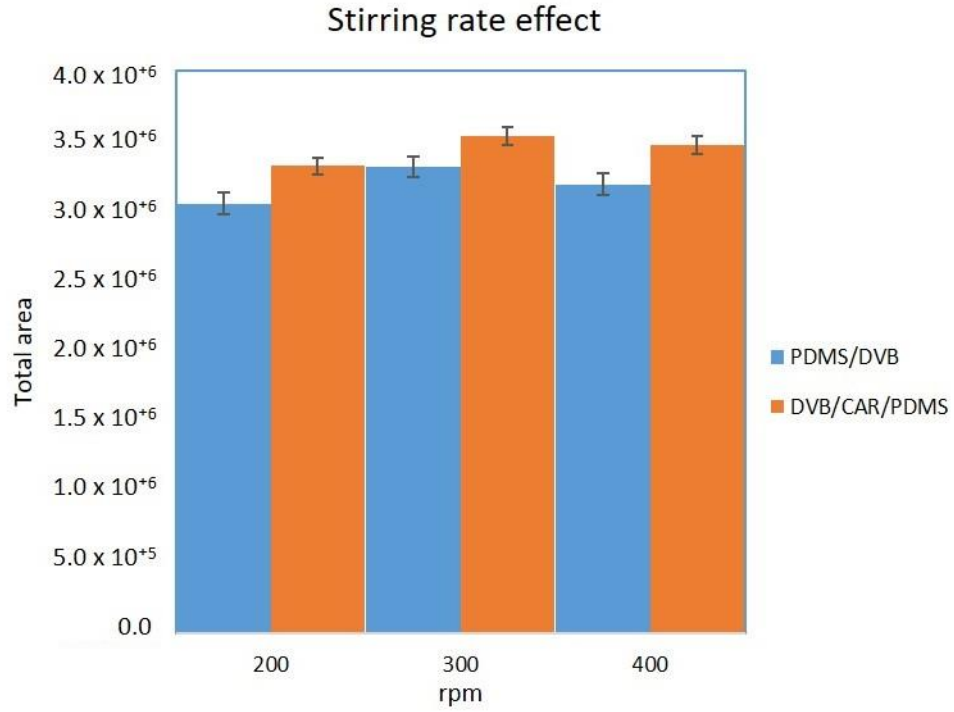

Figure S8. Influence of stirring rate on SPME method extraction optimization.

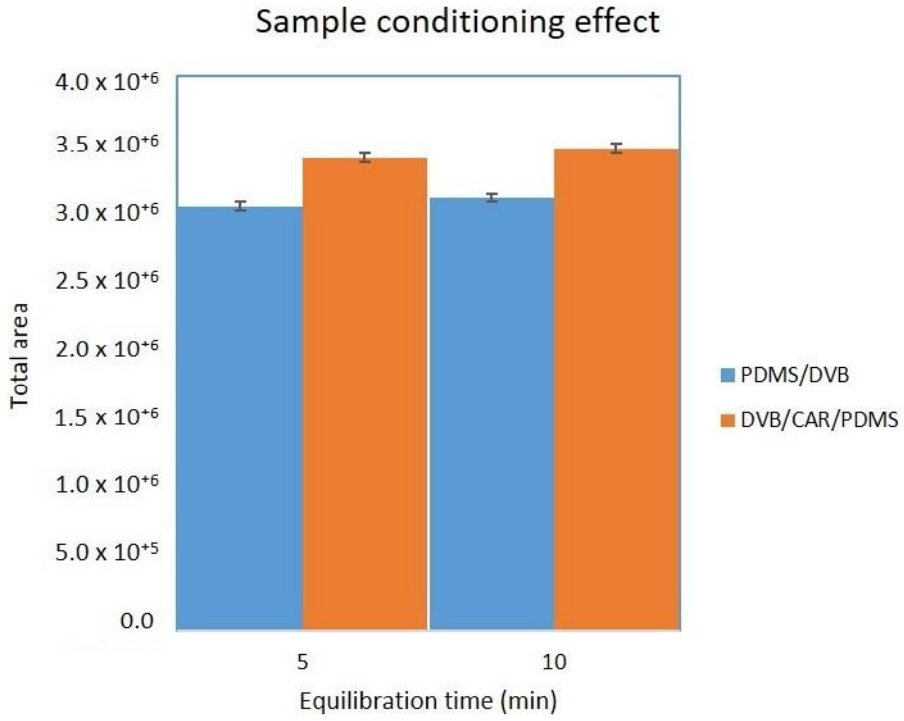

Figure S9. Influence of sample time conditioning on SPME method extraction optimization.

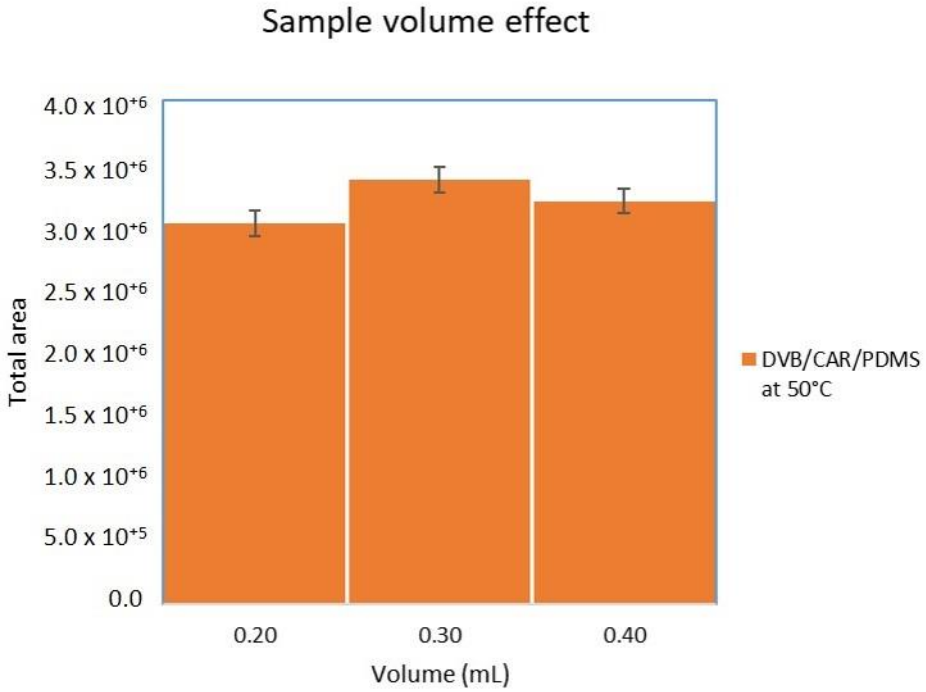

Figure S10. Influence of sample volume on SPME method extraction optimization.

Chili pepper sensorial analysis	
Fresh Fruity and Floral Notes	Fruity
	Apricot
	Watermelon
	Melon
	Banana
	Cherry
	Yellow apple
	green apple
	Pear
	Kiwi
	Citrus fruits
	Grapefruit
	Tropical fruit
	Pineapple
	Mango
	Litchi
	Floral
	Geranium
	Marigold
	Pink
	Iris - Violet
Fresh Vegetable Notes	Grass cut
	Galbanum
	Boxwood
	Artichoke
	Kale
	Thistle
	Cucumber
	Rue
	Tomato leaf
	Ripe pepper
	Green pepper
	Irritating
	Mustard, pungent
	Horseradish (Cren)
	Ginger
	Rapanelli
Dry Vegetable Notes	Paprika
	Dried tomato
	Hay, dry grass
	Black tea
	Walnut husk
	Dry leaves
	Tobacco
Other notes	Brine
	Smoked
	Fat green, oily
	Spicy
	Cinnamon
	Coriander
	Bitter almond
	Vanilla
	Chocolate
	Gaultheria
	Aromatic wood
	Caramel
	Fruit in syrup
	Concentrated tomato
	Fermented
	Dairy, cream, milk
	Blue cheese

Figure S11. List of descriptors used in the sensory analysis of chili peppers