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Characterization of volatile compounds of *Daucus crinitus* Desf. Headspace Solid Phase Microextraction as alternative technique to Hydrodistillation

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Abstract

Background: Traditionally, the essential oil of aromatic herbs is obtained using hydrodistillation (HD). Because the emitted volatile fraction plays a fundamental role in a plant's life, various novel techniques have been developed for its extraction from plants. Among these, headspace solid phase microextraction (HS-SPME) can be used to obtain a rapid fingerprint of a plant's headspace. *Daucus crinitus* Desf. is a wild plant that grows along the west coast of Algeria. Only a single study has dealt with the chemical composition of the aerial part oils of Algerian *D. crinitus*, in which isochavicol isobutyrate (39.0%), octyl acetate (12.3%), and β -caryophyllene (5.4%) were identified. Using GC-RI and GC-MS analysis, the essential oils and the volatiles extracted from separated organs of *D. crinitus* Desf. were studied using HS-SPME.

Results: GC-RI and GC-MS analysis identified 72 and 79 components in oils extracted using HD and in the volatile fractions extracted using SPME, respectively. Two types of essential oils were produced by the plant: the root oils had aliphatic compounds as the main component (87.0%-90.1%), and the aerial part oils had phenylpropanoids as the main component (43.1%-88.6%). HS-SPME analysis showed a more precise distribution of compounds in the organs studied: oxygenated aliphatic compounds were well represented in the roots (44.3%-84.0%), hydrocarbon aliphatic compounds were in the leaves and stems (22.2%-87.9%), and phenylpropanoids were in the flowers and umbels (47.9%-64.2%). Moreover, HS-SPME allowed the occurrence of isochavicol (29.6 - 34.7%) as main component in *D. crinitus* leaves, but it was not detected in the oils, probably because of its solubility in water.

Conclusions: This study demonstrates that HD and HS-SPME modes could be complimentary extraction techniques in order to obtain the complete characterization of plant volatiles.

Background

Daucus is a genus belonging to the Apiaceae family and consists of about 600 species that are widely distributed around the world. *D. carota* (carrot) is the main species of the *Daucus* genus, and its cultivated form, *Daucus carota* ssp. *sativa*, is one of the most popular root vegetable crops in the world. Carrots have been reported to be endowed with medicinal properties, i.e., hypotensive, diuretic, carminative, stomachic, and antilipemic

properties [1-4]. In Algeria, the *Daucus* genus is represented by species living in dry and uncultivated areas and, among these, *D. crinitus* Desf. syn. and *D. meifolius* Brot. are widespread along the Algerian west coast from Tlemcen to Mascara [5]. *D. crinitus* is characterized by the presence of many subspecies that colonize the sands and cliffs [5]. A survey conducted by herbalists identified that, in folk medicine, a drink made from the roots of *D. crinitus* is used in decoction to expel the placenta after childbirth, and as a tonic.

Although the phytochemistry of the *Daucus* genus has been extensively studied (e.g., flavonoids, carotenoids, polyacetylenes, anthocyanins, and volatile constituents),

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only a single study has dealt with the chemical composition of Algerian *D. crinitus* oil [6]. The oil obtained from the aerial parts is dominated by phenylpropanoid compounds (45.5%), followed by aliphatic compounds (17.1%), and hydrocarbons sesquiterpenes (16.6%). The main components are isochavicol isobutyrate (39.0%), an uncommon phenylpropanoid associated with octyl acetate (12.3%), and β -caryophyllene (5.4%). Moreover, antibacterial and antifungal activities of separated phenylpropanoid esters of the entire oil have been reported.

The essential oils of aromatic herbs are traditionally obtained using hydrodistillation. Because the emitted volatile fraction plays a fundamental role in a plant's life, various novel techniques have been developed for its extraction from plants. Among these, headspace solid phase microextraction (HS-SPME) allows for the rapid fingerprinting of a plant's headspace [7-10], and HS sampling requires the optimization of the extraction parameters to be carried out. As has been previously reported in the literature [9,10], the most effective fibers from vegetable matrices used are those consisting of three polymers: a liquid (PDMS) for the less polar components, and two solids, DVB and CAR, for the more polar components. Several conditions regarding the time and temperature for equilibrium and extraction have been reported, according to the plant material analyzed [7-10].

To obtain a better understanding of the volatiles of *D. crinitus*, we investigated the chemical composition of Algerian *D. crinitus* essential oils extracted using hydrodistillation (HD) from separated organs (i.e., the roots, stems, leaves, flowers, and umbels), and the volatile fractions extracted using HS-SPME from the same plant material. In both cases, the analysis was carried out using gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS).

Results and Discussion

Composition of the essential oils

An analysis of the essential oils from the roots, stems, leaves, flowers, and umbels of *D. crinitus* harvested in four locations (A-D) identified 72 components, which accounted for 90.9%-98.3% of the total number. Their retention indices and relative percentages are shown in Table 1. Among these, 22 nonterpenic compounds, 12 monoterpenes, nine sesquiterpenes, and four diterpenes were identified. Identification of 33 components was performed by comparing their EI-MS and retention indices with those from the laboratory-produced "Arômes" library; 13 components were identified by comparing their EI-MS and apolar retention indices with those reported in commercial or literature libraries.

However, the main component of the oils in the aerial parts of *D. crinitus* (**53**, 84.1%-40.1%) remained unidentified, and its identification was carried out using joint information obtained using data from EI-MS and ^{13}C -NMR spectroscopy. The EI-MS data of **53** were close to those of isochavicol 2-methylbutyrate (4-(prop-(1E)-enyl)phenyl 2-methylbutyrate) **60**, except for the molecular ion ($m/z = 204$ vs. $m/z = 218$, respectively), and for a signal at $m/z = 43$, replacing a peak occurring at $m/z = 57$. These signals suggest the occurrence of an isochavicol-derivative compound that had lost a 14 u fragment from the acyl part. The ^{13}C -NMR spectra acquired from the stem oil from a sample from Bensekrane (**53**, 84.1%) exhibited 10 signals, of which, three had double the intensity, assigned from the DEPT spectra of three quaternary carbon atoms (175.60, 149.65, and 135.59 ppm), and two aromatic methine carbon atoms (121.46 and 126.65 ppm), two unsaturated methine carbon atoms (130.15 and 125.78 ppm) and two methyl carbon atoms (18.43 and 18.93 ppm). These signals confirm the presence of phenylpropanoid compounds, and the formula of $\text{C}_{13}\text{H}_{16}\text{O}_2$ was deduced from the DEPT spectra. The identification of isochavicol isobutyrate was unambiguously established from a comparison of its ^{13}C -NMR spectral data with those reported in the literature [6,11] and from the identification of isochavicol as a corresponding alcohol from the LAH reduction of the Bensekrane stem oil sample.

Concerning the plant chemistry, two types of essential oils were produced by *D. crinitus*. The root oils were mainly composed of aliphatic compounds (87.0%-90.1%), and the aerial part oils (i.e., the leaves, stems, flowers, and umbels) were characterized by the occurrence of phenylpropanoids (43.1%-88.6%). The three main aliphatic compounds in the root oils were: dodecyl acetate **57** (30.3%-48.2%), undecane **17** (14.4%-34.1%), and dodecanal **35** (16.7%-26.3%). It is noticeable that the relative percentage abundance of these compounds differed according to the locality of the sampling; undecane was the major component in the Bensekrane (A) and Sid Abdelli (B) sample oils (34.1% and 30.9%, respectively), whereas dodecyl acetate **57** was identified as the main aliphatic component in the Terni (C) and Beni Snous (D) root oils (48.2% and 42.3%, respectively).

Conversely, in the oils from the aerial parts, the main components were isochavicol esters. These oils were similar qualitatively, but differed in the relative amounts of their major components. We noted that isochavicol isobutyrate **53** was always the major component (84.1%-36.5%), whichever organ was analyzed. The other major components identified were: isochavicol 2-methylbutyrate **60** (1.8%-17.8%), pentadecane **50** (0.4%-15.2%), zizaene **44** (trace-9.2%), and undecane **17** (trace-14.2%). Moreover, except for the stem oil obtained from the

Table 1 Chemical compositions of *Daucus crinitus* Desf. essential oils from Algeria

No. ^a	Components ^f	RI _a ^b	RI _a ^c	RI _p ^d	Roots ^e				Leaves ^e				Stems ^e				Umbels ^e				Flowers ^e			
					A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D	A	B	C	D
1	Nonane	906	902	907	0.9	0.8	-	-	0.6	0.5	0.5	0.6	tr	tr	tr	-	0.5	0.4	0.2	0.3	-	-	0.1	tr
2	α-Pinene	936	931	1015	-	-	-	-	0.5	0.4	0.1	-	-	tr	tr	-	0.9	0.8	0.6	0.9	0.2	0.1	0.2	0.5
3	Sabinene	973	966	1107	-	-	-	-	0.6	0.5	0.6	-	-	-	-	-	0.1	0.3	0.1	tr	0.3	0.4	0.6	0.2
4	β-Pinene *	978	971	1124	-	-	-	-	0.1	0.1	0.1	-	-	-	-	-	0.6	0.4	0.1	tr	0.1	0.3	1	1.5
5	Myrcene	987	981	1141	-	-	-	-	0.6	0.3	0.5	-	0.7	0.7	0.9	0.9	0.1	0.2	0.3	0.4	0.2	0.1	tr	tr
6	Decane	993	998	999	0.1	0.1	-	-	tr	tr	tr	tr	0.1	tr	0.1	0.1	tr	0.1	tr	tr	tr	0.1	0.1	tr
7	p-Cymene	1015	1012	1247	-	-	-	-	0.2	0.1	-	-	0.1	0.1	6	4.2	0.7	0.4	0.3	tr	-	-	-	-
8	1,8-Cineole *	1024	1020	1199	-	-	-	-	0.1	0.1	tr	tr	tr	-	0.1	-	0.1	0.1	0.2	tr	0.2	0.4	0.3	0.6
9	Limonene	1025	1026	1190	-	-	-	-	0.9	0.6	0.3	-	0.8	0.8	0.9	1.1	1.6	1.2	1.9	2.6	-	-	-	-
10	(E)-β-Ocimene	1041	1037	1224	-	-	-	-	0.6	0.3	0.2	-	0.1	tr	1.1	1.6	0.2	0.1	0.1	tr	-	-	-	-
11	γ-Terpinene	1051	1049	1228	-	-	-	-	1.6	0.8	0.1	-	0.1	0.1	0.2	0.5	0.3	0.2	0.2	tr	-	-	-	-
12	1-Octanol	1061	1056	1390	-	-	-	-	tr	tr		tr	0,1	0,1	0,1	tr	0,2	0,2	0,1	0,1	tr	tr	-	-
13	2-Methyl-decane	1068	1065	1146	0.1	0.4	-	-	tr	tr	0.1	0.3	-	-	-	-	-	-	-	-	-	-	-	-
14	Nonanal	1076	1074	1403	-	-	-	-	-	0.2	tr	-	tr	0,1	0,2	0,1	0,1	0,1	0,1	0,1	-	-	-	-
15	α-Terpinolene	1082	1079	1274	-	-	-	-	0.4	0.2	0.1	-	0.3	0.3	0.5	0.4	0.3	0.1	0.2	0.1	0.1	0.2	0.4	0.3
16	Linalool *	1086	1086	1528	-	-	-	-	0.2	0.1	tr	-	tr	tr	tr	0.1	0.1	0.2	0.1	tr	tr	0.1	0.1	0.2
17	Undecane	1100	1098	1101	34.1	30.9	14.4	15.3	4.1	5.1	4.5	14.2	tr	0.3	0.3	0.4	0.3	0.5	0.4	0.6	0.1	0.3	0.2	0.1
18	2-Ethyl hexyl acetate *	1144	1149	1420	-	-	-	-	tr	tr	0.1	tr	0.1	tr	0.2	0.1	-	-	tr	0.1	-	0.2	0.2	0.5
19	Terpinen 4-ol	1164	1161	1586	-	-	-	-	0.1	0.1	tr	-	tr	0.1	0.3	0.4	0.3	0.3	0.1	tr	-	-	-	tr
20	Octyl acetate *	1188	1187	1460					2.3	3.0	2.8	1.0	0.2	1.0	1.9	2.5	1.0	1.2	2.2	2.4				
21	Decanal	1188	1187	1483	0.3	0.2	-	-	1.4	1.0	1.4	0.1	tr	0.1	0.3	1	0.6	0.2	1.0	1.2	-	-	-	0.1
22	Dodecane	1200	1198	1209	0,1	0,2	tr	0,1	tr	tr	-	-	0,1	0,1	0,2	tr	-	-	-	-	-	-	-	-
23	Decanol	1263	1259	1729	-	-	tr	0,1	0,1	0,2	0,3	0,1	0,1	0,2	0,1	0,1	-	-	-	-	0,2	0,1	tr	tr
24	Nonanoic acid	1263	1263	2119	-	-	-	-	-	-	-	-	0,1	0,1	0,2	0,1	-	-	-	-	0,1	0,1	0,1	0,1
25	Undecanal	1290	1280	1610	tr	0,1	0,1	-	tr	tr	tr	0,1	0,2	0,1	0,1	tr	0,2	tr	tr	tr	-	-	-	-
26	Tridecane	1300	1292	1305	0.7	0.5	0.9	0.4	0.1	tr	0.1	0.6	0.1	tr	0.1	0.2	0.2	0.5	0.4	0.5	0.1	0.2	0.1	tr
27	n-Octyl isobutyrate	1329	1325	1535	-	-	-	-	tr	0,1	0,1	0,1	-	-	-	-	0.2	0.1	0.2	0.2	0.1	0.1	0.1	0.1
28	Neryl acetate	1342	1336	1730	-	-	-	tr	-	-	tr	tr	0,1	0,2	0,4	0,2	0,1	0,1	0,1	0,1	0,1	tr	tr	0,1
29	Decanoic acid	1347	1348	2080	tr	0,1	tr	tr	-	-	-	-	-	0,1	0,1	tr	0,1	0,1	tr	0,3	-	-	-	-
30	Benzyl 2-methyl butyrate	1360	1352	1770	-	0,2	-	tr	tr	-	-	-	-	-	-	-	-	-	-	-	0,1	0,2	0,1	0,1
31	Geranyl acetate	1362	1359	1759	-	-	-	-	-	-	-	-	-	0,2	0,1	0,1	0,1	0,1	0,1	0,1	0,2	0,1	0,1	0,2
32	Undecanol *	1363	1367	1816	-	-	-	-	0.1	0.1	tr	0.1	0.1	0.1	0.3	0.4	0.4	0.2	0.1	tr	0.2	0.4	0.2	0.6
33	α-Copaene	1379	1372	1470	-	-	-	-	tr	tr	tr	tr	tr	0.1	0.2	0.4	0.5	0.4	0.3	0.2	0.1	0.1	0.1	0.1
34	β-Bourbonene	1386	1376	1520	-	-	-	-	-	-	-	-	0,1	0,5	0,4	0,1	-	-	-	-	-	-	-	-
35	Dodecanal	1389	1390	1695	16.7	24.6	25.1	26.3	3.1	2.1	2.1	6.7	0.5	4.0	5.0	6.1	0.1	tr	0.1	tr	-	0.1	0.1	tr
36	Tetradecane	1400	1403	1408	-	-	-	-	tr	0,1	0,1	0,1	0,1	0,1	0,2	0,1	tr	tr	tr	tr	-	-	-	-

Table 1 Chemical compositions of *Daucus crinitus* Desf. essential oils from Algeria (Continued)

37	Longifolene	1411	1409	1575	-	-	-	-	tr	tr	0,1	tr	0,1	0,1	0,1	-	-	-	-	0,1	0,1	0,1	0,1	
38	α -Santalene	1422	1415	1569	-	-	-	-	-	-	-	-	tr	0,1	0,1	0,2	-	-	-	-	tr	tr	tr	tr
39	β -Caryophyllene	1420	1424	1555	-	-	-	-	0.6	0.4	0.1	0.2	tr	0.4	0.3	0.1	5.4	3.2	3.9	5.1	0.2	0.1	tr	0.1
40	Dauca-3,8-diene	1428	1426	1680	-	-	-	-	tr	tr	tr	0,1	-	-	-	-	-	-	-	0,2	tr	0,1	tr	
41	<i>trans</i> - α -Bergamotene	1432	1432	1575	-	-	-	-	0,1	0,1	tr	tr	0,1	0,3	0,1	tr	-	-	-	tr	0,2	tr	0,1	0,1
42	(E)- β -Farnesene	1446	1443	1660	-	-	-	-	tr	tr	tr	0,1	0,1	0,1	0,2	tr	tr	tr	0,1	tr	0,2	0,2	0,1	0,2
43	α -Humulene	1455	1451	1648	-	-	-	-	0.7	1.0	1.1	0.2	tr	0.2	0.3	0.2	0.5	0.5	0.6	0.3	tr	0.1	tr	0.2
44	Zizaene *	1456	1463	1860	1.2	1.3	2.9	2.7	tr	tr	tr	1.4	1.0	1.1	1.0	1.0	5.9	5.2	6.0	9.2	6.2	8.1	9.1	8.0
45	Dodecanol	1472	1470	1754	0.2	0.2	-	-	tr	tr	0.1	tr	tr	tr	0.1	tr	tr	0.1	0.1	tr	0.2	0.1	0.1	tr
46	α -Curcumene	1473	1474	1769	-	-	-	-	-	-	-	-	0,1	0,1	0,2	0,2	0,1	0,2	0,2	0,1	0,2	tr	tr	tr
47	Germacrene-D	1479	1478	1710	-	-	-	-	tr	tr	0.1	0.1	0.1	0.5	tr	tr	0.2	0.2	0.1	tr	0.2	0.1	tr	0.2
48	β -Selinene *	1486	1480	1685	-	-	-	-	tr	tr	0.2	0.2	-	0.1	tr	0.1	0.1	0.1	0.2	tr	tr	0.1	tr	0.1
49	Zingiberene	1489	1483	1717	-	-	-	-	-	-	-	-	tr	tr	0,1	tr	-	-	-	tr	0,1	tr	tr	0,1
50	Pentadecane	1500	1497	1502	-	-	-	-	5.1	3.5	4.1	2.2	3.0	6.0	12.6	14.5	8.5	9.5	10.5	15.2	4.1	6.2	7.3	10.1
51	δ -Cadinene	1520	1514	1736	-	-	-	-	tr	tr	0.3	0.1	0.1	0.3	tr	0.1	0.6	0.4	0.3	0.4	-	0.1	tr	0.1
52	Geranyl butyrate	1534	1530	1877	-	0,1	tr	0,1	-	-	-	-	tr	0,1	0,2	0,2	-	0,1	tr	0,1	0,2	tr	tr	0,1
53	Isochavicol isobutyrate	1546	1541	2134	-	-	-	-	44.9	35.2	35.6	25.2	84.1	57.6	41.2	36.5	51.2	50.2	50.2	40.1	65.3	55.3	58.2	62.3
54	(Z)-3-Hexenyl benzoate*	1545	1557	2059	1.9	2.3	0.1	0.1	0.1	0.2	0.1	0.1	0.1	0.4	0.2	0.1	0.5	0.6	0.5	0.6	0.1	0.2	0.3	tr
55	Dodecanoic acid *	1554	1560	2474	1.9	0.3	-	-	1.1	12.3	9.3	5.6	0.1	tr	0.6	1.2	0.5	0.3	0.3	0.2	0.1	0.2	0.6	0.3
56	Caryophyllene oxyde	1578	1572	1980	-	-	-	-	-	-	-	-	tr	tr	tr	tr	tr	tr	0,1	0,1	-	-	-	-
57	Dodecyl acetate	1585	1580	1882	31.7	30.3	48.2	42.3	2.5	1.5	7.2	8.9	0.3	0.2	1.9	2.3	tr	0.1	tr	0.1	1.5	1.6	1.8	1.0
58	α -Cedrol	1603	1596	2115	-	-	-	-	tr	tr	0.2	0.1	tr	tr	0.1	tr	tr	tr	tr	tr	0,1	tr	tr	tr
59	Hexadecane	1600	1599	1598	-	-	-	-	0,1	0,1	0,1	0,2	0,2	0,1	0,1	0,1	tr	tr	tr	0,1	tr	0,1	0,1	tr
60	Isochavicol 2-methyl butyrate	1651	1648	2255	0.2	0.3	1.5	2.3	9.7	8.9	11.3	17.8	4.2	7.8	9.1	13.2	3.2	6.5	5.5	6.1	9.8	12.5	9.6	4.8
61	α -Bisabolol *	1673	1667	2202	-	-	-	-	tr	0.1	1.6	0.2	tr	0.1	0.1	tr	0.1	0.1	0.1	0.1	0.2	0.2	0.1	tr
62	Heptadecane	1700	1703	1699	0.2	0.2	-	-	3.4	2.4	6.2	2.1	0.4	6.5	2.5	2.7	5.8	4.8	3.9	4.1	2.5	1.9	2.4	1.1
63	Benzyl benzoate	1730	1723	2121	0,1	0,1	0,2	tr	0,1	0,2	0,1	0,1	0,1	0,2	0,2	0,2	tr	0,1	tr	tr	tr	0,1	tr	tr
64	Tetradecanoic acid *	1761	1756	2649	0.3	0.2	1.1	2.0	3.1	4.4	0.2	0.8	0.1	0.3	0.7	0.4	0.1	0.5	0.5	0.2	0.3	1.0	2.3	2.0
65	Lactarazulene *	1796	1792	2430	0.1	0.4	2.7	0.4	0.7	0.5	0.1	tr	tr	0.8	tr	0.1	-	-	-	-	-	-	0.1	tr
66	Hexadecanal	1782	1787	2108	0.3	0.2	0.2	0.3	0.1	0.6	tr	0.2	0.1	tr	0.1	0.2	0.1	0.2	0.1	tr	-	0.1	0.3	tr
67	Neophytadiene	1807	1807	1918	-	-	-	-	0.4	0.4	0.5	0.1	tr	tr	0.1	0.3	-	-	-	-	-	0.4	0.8	0.4
68	Phytone *	1833	1835	2131	-	-	-	-	tr	0.7	0.3	tr	tr	-	-	-	-	-	-	-	-	-	-	-
69	Dodecyl pentanoate *	1843	1840	2834	0.5	0.2	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
70	Isophytol *	1946	1944	2316	-	-	-	-	tr	tr	0.6	1.1	tr	-	-	-	-	-	-	-	tr	-	-	-
71	Hexadecanoic acid *	1951	1949	2916	0.6	-	-	-	1.1	0.5	0.3	0.1	tr	-	-	-	-	-	-	-	0.2	-	-	-
72	(E)-Phytol *	2114	2102	2620	-	-	-	-	1.7	1.9	2.5	0.7	0.2	-	-	-	-	-	-	-	2.3	-	-	-
Total					92.2	94.2	97.4	92.4	93.2	90.9	93.8	91.9	98.3	92.5	92.4	95.1	92.7	91.4	91.1	92.3	96.9	92.3	97.5	96.6
Hydrocarbon compounds					37.5	34.8	20.9	18.9	21.4	17.4	20.2	22.8	7.5	19.7	28.8	29.7	33.4	29.7	30.9	40.1	15.4	19.2	23.0	23.5
Oxygenated compounds					54.7	59.4	76.5	73.5	71.8	73.5	76.2	69.1	90.8	72.8	63.6	65.4	59.3	61.7	60.2	52.2	81.5	73.1	74.6	73.1

Table 1 Chemical compositions of *Daucus crinitus* Desf. essential oils from Algeria (Continued)

Aliphatic compounds	88.8	89.9	90.1	87.0	28.4	37.9	39.7	44.2	6.0	19.8	28.6	33.2	19.1	19.5	18.8	26.0	10.3	13.1	16.7	19.5
Phenylpropanoid compounds	2.1	2.6	1.7	2.3	54.7	44.3	47.0	43.1	88.6	65.8	50.5	49.8	54.9	57.3	56.2	46.8	75.2	68.0	68.1	64.1
Hydrocarbon non-terpenic compounds	36.2	33.1	15.3	15.8	13.4	11.7	15.7	20.3	4.0	13.0	16.0	18.1	15.8	15.8	15.4	20.8	6.8	16.8	10.2	11.3
Hydrocarbon monoterpenes	-	1.7	-	-	5.5	3.3	2.0	-	2.1	2.0	9.6	8.7	4.8	3.7	3.8	4.0	0.9	1.1	2.3	2.5
Hydrocarbon sesquiterpenes	1.3	-	5.6	3.1	2.1	2.0	2.0	2.4	1.4	4.7	3.1	2.6	12.8	10.2	11.7	15.3	7.7	9.0	9.7	9.3
Hydrocarbon diterpenes	-	-	-	-	0.4	0.4	0.5	0.1	-	-	0.1	0.3	-	-	-	-	-	0.4	0.8	0.4
Oxygenated non-terpenic compounds	54.7	59.4	76.5	73.5	69.7	70.5	71.0	67.0	90.6	72.6	63.1	64.9	58.7	61.0	59.6	52.0	78.7	72.4	74.1	72.3
Oxygenated monoterpenes	-	-	-	-	0.4	0.3	-	-	-	0.1	0.4	0.5	0.5	0.6	0.4	-	0.2	0.5	0.4	0.8
Oxygenated sesquiterpenes	-	-	-	-	-	0.1	1.8	0.3	-	0.1	0.1	-	0.1	0.1	0.2	0.2	0.3	0.2	0.1	-
Oxygenated diterpenes	-	-	-	-	1.7	2.6	3.4	1.8	0.2	-	-	-	-	-	-	-	2.3	-	-	-

^a Order of elution is given on apolar column (Rtx-1). The compounds with an asterisk (*) were only identified in the essential oils.

^b Retention indices of literature on the apolar column (RIa) reported from [12-18].

^c Retention indices on the apolar Rtx-1 column (RIa).

^d Retention indices on the polar Rtx-Wax column (RIp).

^e Percentages are given on the apolar column except for components with identical RIa (percentages are given on the polar column), tr = trace (< 0.05%). Sample locations: Bensekrane (A), Sid Abdeli (B), Terni (C) and Beni Snous (D).

^f Compounds identified from commercial data libraries: National Institute of Standards and Technology, 1999 (12, 33, 39, 43, 44); and König WA, Hochmuth DH, Joulain D, 2001 (26, 34, 35, 36, 40, 41, 42, 46).

Bensekrane (A) sample, it appeared that the sampling locality had a lesser influence on the variability of the component chemicals of the oils. Finally, it should be noted that the relative percentage abundance of the aliphatic and phenylpropanoid compounds was correlated with the position of the organ on the dressed plant. On moving from the bottom to the top of the plant (i.e., the root, leaf, stem, umbel, and then flower), the relative percentage abundance of aliphatic compounds decreased, while the relative percentage abundance of phenylpropanoids increased. In the same way, we noted that the relative percentage abundance of hydrocarbon sesquiterpenes was higher in the umbels and flower oils (10.2%-15.3% and 7.7%-9.7%, respectively) than in the other organs (never more than 5.6%).

HS-SPME analysis of the volatiles

The volatiles emitted from the *D. crinitus* roots, leaves, stems, umbels, and flowers harvested in different locations were investigated using HS-SPME under optimized parameters. The optimization of the HS-SPME sampling parameters was carried out using fresh plant material based on the sum of the total peak areas obtained using GC-FID. The maximum sum of the total peak area was acquired for a temperature of 70°C, an equilibrium time of 60 min, and an extraction time of 30 min (Table 2). The GC-RI and GC-MS analysis

identified 84 components: 45 nonterpenic compounds, 17 monoterpenes, 21 sesquiterpenes, and one diterpene (Tables 3 and 4). Identification of 45 components was performed by comparing their EI-MS and retention indices with those in the laboratory-produced "Arômes" library, and 18 components were identified by comparing their EI-MS data and their apolar retention indices with those reported in commercial or literature libraries.

Regarding the organ contribution to the aromatic plant fingerprint, it should be noted that the volatile constituents were more abundant in the flowers than in the other parts of the plant. Our analysis showed that, for the same organ, the chemical composition of the HS fractions obtained from different localities was qualitatively similar, but differed by the relative percentage abundance of the main components. However, a correlation between the class of compounds and the organ studied was observed: the oxygenated aliphatic compounds were well represented in the roots, hydrocarbon aliphatic compounds were present in the leaves and stems, and phenylpropanoids were present in the flowers and umbels. In particular, the main volatiles from the roots were aliphatic compounds (88.1%-96.3%) such as dodecanal **35** (20.6%-55.4%), undecane **17** (2.3%-43.5%), dodecyl acetate **57** (14.2%-32.4%), and dodecanol **45** (1.7%-8.8%).

Table 2 Influence of HS-SPME parameters (temperature extraction, equilibrium and extraction times) on the volatiles of *Daucus crinitus* Desf

Class of compounds	HS-SPME parameters									
	Equilibrium time t_{eq} min ($T_{ext} = 70^{\circ}C - t_{ext} = 15$ min)				Extraction time t_{ext} min ($T_{ext} = 70^{\circ}C - t_{eq} = 60$ min)		Extraction Temperature T_{ext} °C ($t_{ext} = 30$ min - $t_{eq} = 60$ min)			
	20	40	60	80	30	45	30	50	70	90
Hydrocarbon compounds	37.6	58.8	53.8	49.1	69.3	52.3	85.9	76.3	69.3	62.0
Oxygenated compounds	56.8	37.8	44.8	47.6	30.1	38.1	11.3	22.5	30.1	36.1
Aliphatic compounds	74.6	69.3	78.4	72.2	80.2	67.2	74.8	79.3	80.2	76.1
Phenylpropanoid compounds	2.0	3.2	1.2	2.9	0.6	2.5	0.1	0.3	0.6	0.9
Hydrocarbon non-terpenic compounds	23.5	37.5	39.8	29.9	54.8	33.8	67.4	59.5	54.8	45.1
Hydrocarbon monoterpenes	11.9	17.2	13.1	17.6	6.7	12.1	19.3	12.6	6.7	4.1
Hydrocarbon sesquiterpenes	2.2	4.0	0.6	1.5	7.6	6.3	0.8	4.2	7.6	12.5
Hydrocarbon diterpenes	-	0.1	0.3	0.1	0.2	0.1	-	-	0.2	0.3
Oxygenated non-terpenic compounds	52.9	35.0	39.8	45.2	26.0	35.9	9.1	20.1	26.0	31.9
Oxygenated monoterpenes	3.8	2.8	4.9	2.3	1.0	2.1	2.2	2.2	1.0	0.5
Oxygenated sesquiterpenes	0.1	-	0.1	0.1	3.1	0.1	-	0.2	3.1	3.7
Esters	4.9	5.4	5.4	7.0	9.9	4.5	3.2	8.6	9.9	12.8
Alcohols	4.2	2.8	3.9	2.2	4.4	29.0	1.9	3.2	4.4	7.3
Ketones	0.7	0.1	0.6	0.2	0.4	0.3	0.1	0.2	0.4	0.2
Aldehydes	43.0	25.4	28.0	35.3	10.2	25.6	3.2	8.5	10.2	11.2
Total identification (%)	94.6	96.6	98.6	96.7	99.4	90.4	97.2	98.8	99.4	98.1
Total area 10^5 ^a	223.2	282.8	351.0	303.1	454.1	426.4	96.8	206.4	454.1	451.2

^a Total area is expressed in arbitrary units.

Fresh aerial parts of *Daucus crinitus* Desf. used for this study were harvested in Bensekrane.

Table 3 Volatile components extracted by HS-SPME from roots, leaves and stems of *Daucus crinitus* Desf

No. a	Components ^f	IRIa ^b	RIa ^c	Roots ^d				Leaves ^d				Stems ^d			
				A	B	C	D	A	B	C	D	A	B	C	D
1a	Heptane	700	702	0.3 ± 0.01	tr	-	-	0.1 ± 0.01	tr	tr	tr	0.3 ± 0.07	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
1b	3-methyl 1-Butanol	717	710	-	-	-	-	tr	-	-	-	0.3 ± 0.01	0.1 ± 0.01	0.3 ± 0.01	0.5 ± 0.07
1c	Hexanal	780	767	tr	tr	tr	-	tr	0.1 ± 0.01	tr	0.6 ± 0.07	0.7 ± 0.07	0.2 ± 0.01	0.8 ± 0.07	1.0 ± 0.14
1d	Hex-5-en-1-ol	820	820	-	-	-	-	0.3 ± 0.07	0.5 ± 0.07	0.2 ± 0.01	0.9 ± 0.07	tr	tr	0.1 ± 0.01	0.1 ± 0.01
1e	2-Heptanone	871	870	tr	-	-	-	tr	0.3 ± 0.01	-	0.3 ± 0.01	tr	-	-	-
1	Nonane	906	902	0.3 ± 0.07	5.5 ± 0.21	-	-	3.7 ± 0.14	2.1 ± 0.14	1.2 ± 0.14	0.8 ± 0.14	1.4 ± 0.14	0.5 ± 0.07	1.4 ± 0.21	1.7 ± 0.28
2	α-Pinene	936	931	-	-	-	-	0.2 ± 0.01	2.8 ± 0.21	0.2 ± 0.01	0.6 ± 0.01	6.1 ± 0.21	1.8 ± 0.21	6.1 ± 0.01	2.6 ± 0.14
2a	Camphene	950	943	-	-	-	-	0.1 ± 0.01	-	-	-	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
3	Sabinene	973	966	-	0.1 ± 0.01	-	-	0.3 ± 0.01	0.3 ± 0.01	-	tr	0.6 ± 0.07	0.2 ± 0.01	0.4 ± 0.01	0.3 ± 0.01
3a	2-pentyl Furan	981	978	0.3 ± 0.01	-	-	-	tr	-	-	-	0.2 ± 0.01	tr	0.2 ± 0.01	0.1 ± 0.01
5	Myrcene	987	981	-	-	-	-	0.1 ± 0.01	0.6 ± 0.14	-	0.2 ± 0.07	10.6 ± 0.64	10.0 ± 0.64	7.4 ± 0.54	7.5 ± 0.35
5a	α-Phellandrene	1002	991	-	-	-	-	tr	0.2 ± 0.01	-	-	0.3 ± 0.01	0.4 ± 0.07	0.4 ± 0.01	0.4 ± 0.07
5b	3-methyl butyl Isobutyrate	994	997	-	-	-	-	0.2 ± 0.01	tr	0.1 ± 0.01	-	tr	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
6	Decane	993	998	0.2 ± 0.01	1.2 ± 0.14	0.1 ± 0.01	-	tr	tr	-	-	0.1 ± 0.01	0.3 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
6a	2-methyl butyl Isobutyrate	1004	999	-	-	-	-	0.1 ± 0.01	tr	0.2 ± 0.01	-	0.1 ± 0.01	-	-	tr
7	p-Cymene	1015	1012	-	-	-	-	-	3.5 ± 0.21	-	0.1 ± 0.01	2.2 ± 0.14	0.2 ± 0.01	2.7 ± 0.21	3.3 ± 0.21
9	Limonene	1025	1026	-	0.1 ± 0.01	-	-	0.2 ± 0.01	2.0 ± 0.35	0.2 ± 0.01	0.3 ± 0.07	7.5 ± 0.49	11.7 ± 0.64	9.9 ± 0.49	11.1 ± 0.92
10	(E)-β-Ocimene	1041	1037	-	-	-	-	tr	0.7 ± 0.07	0.1 ± 0.01	tr	0.1 ± 0.01	0.5 ± 0.01	0.4 ± 0.01	0.7 ± 0.01
11	γ-Terpinene	1051	1049	-	-	-	-	0.2 ± 0.01	7.4 ± 0.01	-	-	1.6 ± 0.28	2.7 ± 0.21	1.6 ± 0.01	2.3 ± 0.28
12	1-Octanol	1061	1056	-	-	-	-	0.1 ± 0.01	tr	-	tr	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.07
13	2-methyl Decane	1068	1065	0.4 ± 0.07	6.7 ± 0.71	0.3 ± 0.07	-	0.6 ± 0.07	-	-	-	tr	-	tr	tr
14	Nonanal	1076	1074	-	-	-	-	tr	0.4 ± 0.01	-	-	-	0.3 ± 0.01	0.5 ± 0.01	0.8 ± 0.07
15	α-Terpinolene	1082	1079	-	-	-	-	0.2 ± 0.01	9.4 ± 0.42	-	-	0.2 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.5 ± 0.07
15a	2-Nonanol	1085	1080	-	-	-	0.1 ± 0.01	-	-	-	-	0.1 ± 0.01	0.4 ± 0.01	0.4 ± 0.01	0.5 ± 0.01
17	Undecane	1100	1098	43.5 ± 0.85	5.0 ± 0.35	26.2 ± 0.92	2.3 ± 0.21	11.1 ± 0.57	2.9 ± 0.35	1.2 ± 0.07	8.9 ± 0.28	2.7 ± 0.78	2.8 ± 0.14	2.1 ± 0.35	2.6 ± 0.14
17a	Limonene 1,2-epoxide	1117	1113	-	-	-	-	tr	0.1 ± 0.01	-	-	-	-	-	-
17b	Camphor	1123	1120	-	-	-	-	tr	0.5 ± 0.07	0.3 ± 0.01	0.5 ± 0.07	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
17c	n-hexyl Isobutyrate	1127	1126	-	-	-	-	0.1 ± 0.01	0.1 ± 0.01	-	0.1 ± 0.01	-	0.2 ± 0.01	0.1 ± 0.01	tr
17d	Cryptone	1160	1158	-	-	-	-	tr	0.1 ± 0.01	-	-	0.4 ± 0.07	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01
19	Terpinen-4-ol	1164	1161	-	-	-	-	-	-	-	-	0.3 ± 0.01	0.6 ± 0.07	0.3 ± 0.01	0.4 ± 0.01
19a	3-methyl Undecane	1170	1165	0.1 ± 0.01	0.5 ± 0.07	tr	-	-	-	-	-	-	-	-	-
19b	Estragole	1175	1169	-	-	-	-	0.2 ± 0.01	-	-	-	tr	0.9 ± 0.01	0.8 ± 0.14	1.0 ± 0.14
21	Decanal	1188	1187	-	0.1 ± 0.01	-	-	1.5 ± 0.02	14.8 ± 0.01	7.8 ± 0.57	2.5 ± 0.14	1.1 ± 0.01	1.8 ± 0.21	2.1 ± 0.14	2.5 ± 0.01

Table 3 Volatile components extracted by HS-SPME from roots, leaves and stems of *Daucus crinitus* Desf (Continued)

22	Dodecane	1200	1198	0.3 ± 0.07	0.3 ± 0.01	tr	-	0.1 ± 0.01	tr	-	-	tr	0.3 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
22a	γ-Octanolide	1208	1208	-	-	-	-	0.1 ± 0.01	0.1 ± 0.01	0.5 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.4 ± 0.01	0.3 ± 0.01	0.4 ± 0.07
22b	Chavicol	1219	1214	-	0.1 ± 0.01	-	-	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	-	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.3 ± 0.01
22c	2-Nonanyl acetate	1224	1220	-	0.7 ± 0.01	-	-	-	-	-	-	tr	0.2 ± 0.01	tr	tr
23	Decanol	1263	1259	-	0.1 ± 0.01	-	0.4 ± 0.07	0.2 ± 0.01	0.8 ± 0.01	1.8 ± 0.21	-	1.8 ± 0.14	2.2 ± 0.14	1.4 ± 0.14	1.5 ± 0.21
23a	trans-Anethol	1262	1260	-	-	-	-	tr	-	-	-	tr	0.1 ± 0.01	tr	tr
24	Nonanoic acid	1263	1263	-	0.1 ± 0.01	-	-	-	-	-	-	0.3 ± 0.07	0.4 ± 0.07	0.4 ± 0.01	0.4 ± 0.01
24a	Benzyl isobutyrate	1269	1266	-	-	-	-	-	-	-	-	-	-	-	-
24b	Undecan-2-one	1273	1268	0.1 ± 0.01	tr	-	1.1 ± 0.14	0.1 ± 0.01	-	-	-	0.2 ± 0.01	0.6 ± 0.07	0.5 ± 0.01	0.5 ± 0.01
25	Undecanal	1290	1280	-	0.7 ± 0.21	0.2 ± 0.01	-	-	tr	0.2 ± 0.01	-	tr	0.3 ± 0.01	0.2 ± 0.01	0.3 ± 0.01
26	Tridecane	1300	1292	3.7 ± 0.21	7.7 ± 0.85	4.0 ± 0.35	0.7 ± 0.07	0.2 ± 0.01	0.1 ± 0.01	0.4 ± 0.01	0.3 ± 0.07	0.2 ± 0.01	0.4 ± 0.01	0.3 ± 0.01	0.4 ± 0.01
26a	Isochavicol	1313	1315	-	-	-	-	0.1 ± 0.01	0.1 ± 0.01	0.7 ± 0.01	-	0.4 ± 0.07	0.1 ± 0.01	0.1 ± 0.01	tr
27	n-Octyl isobutyrate	1329	1325	-	-	-	-	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	-	-	-	-	-
28	Neryl acetate	1342	1336	-	-	-	0.6 ± 0.01	-	-	0.1 ± 0.01	-	0.2 ± 0.01	1.1 ± 0.21	1.1 ± 0.01	1.0 ± 0.14
29	Decanoic acid	1347	1348	0.2 ± 0.01	0.4 ± 0.01	0.4 ± 0.01	-	-	-	tr	-	tr	0.2 ± 0.01	0.1 ± 0.01	tr
30	Benzyl 2-methyl butyrate	1360	1352	-	0.6 ± 0.07	-	-	tr	-	tr	-	-	-	-	-
31	Geranyl acetate	1362	1359	-	-	-	-	-	-	0.1 ± 0.01	-	tr	0.2 ± 0.01	0.2 ± 0.01	0.1 ± 0.01
33	α-Copaene	1379	1372	-	-	-	-	-	-	-	-	1.6 ± 0.14	2.1 ± 0.14	4.1 ± 0.01	2.6 ± 0.14
34	β-Bourbonene	1386	1376	-	-	-	-	-	-	-	-	4.0 ± 0.42	3.6 ± 0.21	3.7 ± 0.01	3.2 ± 0.28
35	Dodecanal	1389	1390	29.3 ± 1.2	20.6 ± 1.84	45.1 ± 1.27	55.4 ± 0.99	0.4 ± 0.14	1.5 ± 0.21	4.4 ± 0.14	2.1 ± 0.01	2.7 ± 0.28	1.3 ± 0.21	1.2 ± 0.01	1.4 ± 0.07
36	Tetradecane	1400	1403	-	-	-	-	0.1 ± 0.07	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
37	Longifolene	1411	1409	-	0.2 ± 0.01	tr	-	tr	0.2 ± 0.01	-	2.3 ± 0.21	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
38	α-Santalene	1422	1415	-	-	tr	-	-	-	-	tr	0.1 ± 0.01	tr	tr	tr
39	β-Caryophyllene	1421	1424	-	-	-	-	0.8 ± 0.14	0.1 ± 0.01	-	-	0.7 ± 0.14	1.2 ± 0.07	0.4 ± 0.01	0.8 ± 0.07
40	Dauca-3,8-diene	1428	1426	-	-	-	-	0.1 ± 0.01	-	-	-	-	-	-	-
41	trans-α-bergamotene	1432	1432	-	-	-	-	0.7 ± 0.01	0.2 ± 0.01	-	-	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
42	(E)-β-Farnesene	1446	1443	-	-	-	-	0.1 ± 0.01	0.1 ± 0.01	-	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
43	α-Humulene	1455	1451	-	-	-	-	0.4 ± 0.01	0.3 ± 0.01	1.0 ± 0.01	0.3 ± 0.01	0.9 ± 0.01	0.3 ± 0.01	0.4 ± 0.07	0.4 ± 0.01
45	Dodecanol	1472	1470	2.7 ± 0.01	8.8 ± 0.42	1.7 ± 0.28	4.4 ± 0.35	0.2 ± 0.01	-	-	-	0.5 ± 0.01	0.8 ± 0.21	0.9 ± 0.01	0.5 ± 0.07
46	α-Curcumene	1473	1474	-	-	-	-	-	-	-	-	0.8 ± 0.14	0.6 ± 0.01	0.9 ± 0.01	0.4 ± 0.01
47	Germacrene-D	1479	1478	0.2 ± 0.01	-	-	-	-	-	-	-	0.8 ± 0.01	2.1 ± 0.28	3.3 ± 0.01	2.1 ± 0.07
49	Zingiberene	1489	1483	0.2 ± 0.01	0.7 ± 0.14	0.4 ± 0.07	0.6 ± 0.01	-	-	-	-	tr	0.2 ± 0.01	tr	0.1 ± 0.01
50	Pentadecane	1500	1497	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	51.6 ± 1.77	12.8 ± 0.49	41.2 ± 1.34	40.8 ± 0.57	11.9 ± 1.06	13.1 ± 0.78	14.0 ± 0.28	16.0 ± 0.42
51	δ-Cadinene	1520	1514	-	-	-	-	0.1 ± 0.01	tr	1.1 ± 0.01	0.3 ± 0.01	-	-	-	-
52	Geranyl butyrate	1534	1530	tr	0.1 ± 0.01	-	0.2 ± 0.01	-	0.6 ± 0.01	-	-	0.3 ± 0.01	2.0 ± 0.01	1.7 ± 0.01	1.6 ± 0.21
53	Isochavicol isobutyrate	1546	1541	-	0.4 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	19.9 ± 0.85	10.4 ± 1.13	19.0 ± 0.85	0.2 ± 0.01	0.7 ± 0.14	0.4 ± 0.01	0.2 ± 0.01
56	Caryophyllene oxyde	1578	1572	-	-	-	-	-	-	-	-	0.1 ± 0.01	tr	tr	tr

Table 3 Volatile components extracted by HS-SPME from roots, leaves and stems of *Daucus crinitus* Desf (Continued)

57	Dodecyl acetate	1585	1580	14.2 ± 0.49	32.4 ± 1.70	16.4 ± 1.06	21.7 ± 0.85	0.2 ± 0.01	0.3 ± 0.01	3.6 ± 0.21	5.0 ± 0.21	2.3 ± 0.28	2.0 ± 0.01	2.3 ± 0.21	2.6 ± 0.07
58	α-Cedrol	1603	1596	-	-	-	-	-	0.1 ± 0.01	-	-	1.4 ± 0.21	1.0 ± 0.01	0.9 ± 0.01	0.9 ± 0.07
59	Hexadecane	1600	1599	-	-	-	-	0.3 ± 0.01	0.1 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.5 ± 0.01	0.4 ± 0.01	0.2 ± 0.01	0.3 ± 0.01
60	Isochavicol 2-methyl butyrate	1651	1648	-	-	-	0.4 ± 0.01	0.1 ± 0.01	2.7 ± 0.01	2.9 ± 0.01	2.1 ± 0.14	0.1 ± 0.01	0.4 ± 0.01	0.3 ± 0.01	0.1 ± 0.01
60a	Bisabolol oxide B	1654	1650	-	-	-	-	0.2 ± 0.01	-	tr	0.1 ± 0.01	3.9 ± 0.01	2.7 ± 0.01	2.1 ± 0.01	1.1 ± 0.14
62	Heptadecane	1700	1703	0.1 ± 0.01	0.2 ± 0.01	tr	0.2 ± 0.01	20.7 ± 1.56	4.1 ± 0.21	11.9 ± 0.35	6.4 ± 0.57	20.7 ± 0.57	13.2 ± 0.42	9.0 ± 0.35	11.2 ± 0.49
63	Benzyl benzoate	1730	1723	0.1 ± 0.01	0.7 ± 0.01	tr	2.7 ± 0.14	-	-	0.3 ± 0.01	0.7 ± 0.01	0.5 ± 0.07	0.2 ± 0.01	0.1 ± 0.01	0.2 ± 0.01
66	Hexadecanal	1782	1787	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.07	0.7 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	tr	0.1 ± 0.01	tr	tr	0.2 ± 0.01
67	Neophytadiene	1807	1807	tr	0.8 ± 0.01	tr	3.2 ± 0.21	0.6 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.4 ± 0.01	0.3 ± 0.01	tr	0.1 ± 0.01	0.2 ± 0.01
	% Identification			96.8 ± 0.57	95.4 ± 0.21	95.7 ± 0.28	95.2 ± 0.07	97.3 ± 0.21	93.6 ± 0.64	93.1 ± 0.21	96.3 ± 0.28	95.7 ± 0.35	92.1 ± 0.07	90.9 ± 0.28	92.9 ± 0.49
	Total area (10 ⁵)			486.4	451.3	445.5	430.2	391.8	351.9	378.3	345.6	312.5	336.1	333.8	342.8
	Hydrocarbon compounds			49.4	28.4	31.2	7.3	92.8	65.1	66.9	65.4	82.8	72.9	73.9	76.4
	Oxygenated compounds			47.4	67.0	64.5	87.9	4.5	28.5	26.2	30.9	12.9	19.2	17.0	16.5
	Aliphatic compounds			96.3	91.8	95.1	88.1	90.8	42.0	75.7	69.3	49.4	46.1	42.6	49.1
	Phenylpropanoid compounds			0.1	1.8	0.2	3.3	0.7	22.8	14.4	21.8	1.3	2.5	1.9	1.8
	Hydrocarbon non-terpenic compounds			49.0	27.4	30.8	3.5	88.7	37.1	64.2	60.8	43.8	34.2	31.3	37.3
	Hydrocarbon monoterpenes			-	0.2	-	-	1.3	26.9	0.5	1.2	29.4	28.0	29.4	28.9
	Hydrocarbon sesquiterpenes			0.4	0.8	0.4	0.6	2.2	0.9	2.1	3.0	9.3	10.7	13.1	10.0
	Hydrocarbon diterpenes			-	-	-	3.2	0.6	0.2	0.1	0.4	0.3	-	0.1	0.2
	Oxygenated non-terpenic compounds			47.4	66.2	64.5	87.9	4.3	27.7	25.9	30.3	6.9	14.4	13.2	13.6
	Oxygenated monoterpenes			-	-	-	-	-	0.7	0.3	0.5	0.8	1.1	0.8	0.9
	Oxygenated sesquiterpenes			-	0.8	-	-	0.2	0.1	-	0.1	5.2	3.7	3.0	2.0

^a Order of elution is given on apolar column (Rtx-1). Numbers correspond to those in table 1. The compounds that the number is followed by a letter were only identified in HS-fractions.

^b Retention indices of literature on the apolar column (RIa) reported from [12-18].

^c Retention indices on the apolar Rtx-1 column (RIa).

^d Percentages (means of three analyses) obtained by GC-FID (on RTX-1: apolar column) with peak-area normalization under optimized HS-SPME parameters: temperature: 70°C; equilibrium time: 60 min; extraction time: 30 min. Sample locations: Bensekrane (A), Sid Abdeli (B), Terni (C) and Beni Snous (D).

^e Total area is expressed in arbitrary units.

^f Compounds identified from commercial data libraries: National Institute of Standards and Technology, 1999 (1b, 12, 15c, 17a, 19d, 20b); and literature data: König WA, Hochmuth DH, Joulain D, 2001 (3a, 13a, 19b, 19c, 24a, 32b, 35, 36, 36a, 38a, 41, 42).

Table 4 Volatile components extracted by HS-SPME from umbels and flowers of *Daucus crinitus* Desf

No. ^a	Components ^f	/RI _a ^b	RI _a ^c	Umbels ^d				Flowers ^d			
				A	B	C	D	A	B	C	D
1a	Heptane	700	702	tr	tr	0.1 ± 0.01	tr	tr	0.1 ± 0.01	tr	tr
1b	3-methyl 1-Butanol	717	710	tr	tr	0.1 ± 0.01	0.1 ± 0.01	-	-	-	-
1c	Hexanal	780	767	0.1 ± 0.01	0.1 ± 0.01	tr	tr	0.2 ± 0.01	0.3 ± 0.07	0.6 ± 0.01	0.8 ± 0.01
1d	Hex-5-en-1-ol	820	820	tr	tr	tr	0.1 ± 0.01	-	-	-	-
1e	2-Heptanone	871	870	-	-	-	-	-	-	-	-
1	Nonane	906	902	0.2 ± 0.07	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.5 ± 0.07	0.4 ± 0.07
2	α-Pinene	936	931	0.2 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.7 ± 0.07	0.5 ± 0.14	0.7 ± 0.01	0.8 ± 0.01
2a	Camphene	950	943	0.1 ± 0.01	-	-	-	-	-	-	-
3	Sabinene	973	966	-	-	-	-	-	-	-	-
3a	2-pentyl Furan	981	978	0.1 ± 0.01	-	-	-	-	-	-	-
5	Myrcene	987	981	0.6 ± 0.01	0.2 ± 0.01	0.6 ± 0.07	0.2 ± 0.01	0.6 ± 0.01	0.5 ± 0.07	2.2 ± 0.14	2.1 ± 0.07
5a	α-Phellandrene	1002	991	1.1 ± 0.01	-	-	-	-	-	-	-
5b	3-methyl butyl Isobutyrate	994	997	0.5 ± 0.07	0.3 ± 0.01	0.6 ± 0.07	0.7 ± 0.07	0.4 ± 0.01	0.3 ± 0.01	0.4 ± 0.07	0.3 ± 0.01
6	Decane	993	998	tr	tr	0.1 ± 0.01	tr	-	-	-	-
6a	2- methyl butyl Isobutyrate	1004	999	-	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
7	p-Cymene	1015	1012	0.8 ± 0.07	9.7 ± 0.14	0.6 ± 0.01	0.6 ± 0.07	0.2 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.2 ± 0.01
9	Limonene	1025	1026	1.8 ± 0.21	1.6 ± 0.07	1.8 ± 0.14	2.3 ± 0.28	0.7 ± 0.14	0.7 ± 0.07	1.1 ± 0.14	2.2 ± 0.28
10	(E)-β-Ocimene	1041	1037	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	tr	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
11	γ-Terpinene	1051	1049	0.4 ± 0.07	0.7 ± 0.14	0.5 ± 0.01	0.4 ± 0.01	0.1 ± 0.01	tr	0.1 ± 0.01	0.1 ± 0.01
12	1-Octanol	1061	1056	0.2 ± 0.01	0.6 ± 0.07	0.5 ± 0.01	0.6 ± 0.07	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01
13	2-methyl Decane	1068	1065	-	-	-	-	-	-	-	-
14	Nonanal	1076	1074	0.3 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.07	-	-	-	-
15	α-Terpinolene	1082	1079	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	-	-	-	-
15a	2-Nonanol	1085	1080	tr	0.1 ± 0.01	0.1 ± 0.01	tr	-	-	-	-
17	Undecane	1100	1098	0.3 ± 0.07	0.3 ± 0.01	0.3 ± 0.01	0.2 ± 0.07	0.1 ± 0.01	tr	0.1 ± 0.01	0.1 ± 0.01
17a	Limonene 1-2-epoxide	1117	1113	tr	tr	-	tr	tr	0.2 ± 0.01	0.1 ± 0.01	tr
17b	Camphor	1123	1120	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	tr	0.1 ± 0.01	-	tr
17c	n-hexyl Isobutyrate	1127	1126	0.5 ± 0.07	0.5 ± 0.01	0.5 ± 0.01	0.6 ± 0.14	-	-	-	-
17d	Cryptone	1160	1158	tr	tr	0.1 ± 0.01	tr	tr	tr	0.1 ± 0.01	0.1 ± 0.01
19	Terpinen-4-ol	1164	1161	tr	tr	-	0.1 ± 0.01	tr	0.2 ± 0.01	0.3 ± 0.01	0.1 ± 0.01
19a	3-methyl Undecane	1170	1165	-	-	-	-	-	-	-	-
19b	Estragole	1175	1169	0.1 ± 0.01	0.4 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	-	-	-	-
21	Decanal	1188	1187	tr	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	-	-	-	-
22	Dodecane	1200	1198	-	-	-	-	-	-	-	-
22a	γ-Octanolide	1208	1208	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.4 ± 0.07
22b	Chavicol	1219	1214	2.3 ± 0.28	1.7 ± 0.01	2.0 ± 0.14	1.7 ± 0.28	tr	0.1 ± 0.01	0.1 ± 0.01	tr

Table 4 Volatile components extracted by HS-SPME from umbels and flowers of *Daucus crinitus* Desf (Continued)

22c	2-Nonanyl acetate	1224	1220	tr	tr	-	0.1 ± 0.01	0.7 ± 0.14	0.9 ± 0.01	0.7 ± 0.01	0.8 ± 0.14
23	Decanol	1263	1259	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.07	0.5 ± 0.07	0.2 ± 0.01	0.4 ± 0.01	0.4 ± 0.07
23a	Trans-Anethol	1262	1260	0.5 ± 0.01	tr	0.1 ± 0.01	0.5 ± 0.07	0.4 ± 0.01	0.3 ± 0.07	0.6 ± 0.01	0.5 ± 0.01
24	Nonanoic acid	1263	1263	2.3 ± 0.21	0.2 ± 0.07	-	-	0.5 ± 0.14	0.5 ± 0.07	0.7 ± 0.07	0.4 ± 0.01
24a	Benzyl isobutyrate	1269	1266	-	-	-	-	0.3 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.5 ± 0.01
24b	Undecan-2-one	1273	1268	0.2 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.2 ± 0.01	0.4 ± 0.01	0.2 ± 0.01
25	Undecanal	1290	1280	0.3 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.4 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.4 ± 0.01
26	Tridecane	1300	1292	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.0	0.1 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01
26a	Isochavicol	1313	1315	15.2 ± 1.34	9.1 ± 0.57	15.5 ± 0.42	7.1 ± 0.49	31.8 ± 1.34	34.7 ± 1.27	29.6 ± 0.99	32.9 ± 1.13
27	n-Octyl isobutyrate	1329	1325	0.4 ± 0.07	0.2 ± 0.01	0.3 ± 0.01	0.2 ± 0.01	0.8 ± 0.07	0.7 ± 0.01	0.4 ± 0.01	0.5 ± 0.01
28	Neryl acetate	1342	1336	0.2 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
29	Decannoic acid	1347	1348	0.2 ± 0.01	tr	0.1 ± 0.01	0.1 ± 0.01	-	-	-	-
30	Benzyl 2-methyl butyrate	1360	1352	tr	0.2 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.3 ± 0.01	0.1 ± 0.01	0.5 ± 0.01	0.3 ± 0.01
31	Geranyl acetate	1362	1359	0.7 ± 0.14	0.7 ± 0.07	0.7 ± 0.07	0.7 ± 0.07	0.6 ± 0.07	0.3 ± 0.01	0.2 ± 0.01	0.7 ± 0.01
33	α -Copaene	1379	1372	0.3 ± 0.14	0.4 ± 0.01	0.5 ± 0.01	0.4 ± 0.01	0.6 ± 0.14	0.4 ± 0.01	0.6 ± 0.01	0.6 ± 0.07
34	β -Bourbonene	1386	1376	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.2 ± 0.01	0.1 ± 0.01
35	Dodecanal	1389	1390	0.4 ± 0.07	0.6 ± 0.01	0.6 ± 0.01	0.5 ± 0.07	0.5 ± 0.14	0.5 ± 0.01	0.8 ± 0.14	0.4 ± 0.01
36	Tetradecane	1400	1403	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
37	Longifolene	1411	1409	tr	tr	tr	tr	0.6 ± 0.01	0.5 ± 0.01	0.7 ± 0.01	0.3 ± 0.07
38	α -Santalene	1422	1415	-	-	-	-	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01
39	β -Caryophyllene	1421	1424	5.1 ± 0.28	5.8 ± 0.01	4.2 ± 0.14	5.4 ± 0.42	0.1 ± 0.01	tr	0.2 ± 0.01	tr
40	Dauca-3,8-diene	1428	1426	tr	tr	tr	tr	0.2 ± 0.01	0.1 ± 0.10	0.3 ± 0.07	0.5 ± 0.07
41	Trans- α -bergamotene	1432	1432	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.2 ± 0.01	0.7 ± 0.07	0.4 ± 0.07	0.6 ± 0.07	0.5 ± 0.07
42	(E)- β -Farnesene	1446	1443	0.4 ± 0.01	tr	0.3 ± 0.01	0.2 ± 0.01	0.7 ± 0.07	0.5 ± 0.07	1.1 ± 0.01	0.7 ± 0.01
43	α -Humulene	1455	1451	tr	0.4 ± 0.01	0.1 ± 0.01	0.2 ± 0.07	0.3 ± 0.01	0.3 ± 0.01	0.3 ± 0.01	0.1 ± 0.01
45	Dodecanol	1472	1470	6.0 ± 0.14	6.8 ± 0.49	7.1 ± 0.35	7.6 ± 0.42	1.9 ± 0.28	3.6 ± 0.14	2.6 ± 0.07	2.0 ± 0.14
46	α -Curcumene	1473	1474	0.8 ± 0.21	tr	0.5 ± 0.01	0.3 ± 0.01	0.5 ± 0.05	0.4 ± 0.01	0.7 ± 0.07	0.3 ± 0.01
47	Germacrene-D	1479	1478	0.2 ± 0.01	1.0 ± 0.01	0.9 ± 0.01	0.7 ± 0.07	0.5 ± 0.01	0.2 ± 0.01	0.5 ± 0.01	0.5 ± 0.01
49	Zingiberene	1489	1483	tr	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.5 ± 0.01	0.3 ± 0.01	0.8 ± 0.07	0.4 ± 0.01
50	Pentadecane	1500	1497	8.9 ± 0.57	5.9 ± 0.20	4.1 ± 0.28	3.6 ± 0.21	14.2 ± 0.49	12.5 ± 0.35	14.0 ± 0.64	12.9 ± 0.49
51	δ -cadinene	1520	1514	0.8 ± 0.01	0.1 ± 0.01	0.6 ± 0.01	0.7 ± 0.07	0.5 ± 0.01	0.2 ± 0.01	0.4 ± 0.01	0.4 ± 0.01
52	Geranyl butyrate	1534	1530	tr	0.4 ± 0.01	0.5 ± 0.01	0.4 ± 0.07	tr	0.1 ± 0.01	tr	0.1 ± 0.01
53	Isochavicol isobutyrate	1546	1541	26.7 ± 1.20	49.4 ± 0.99	40.3 ± 1.70	51.8 ± 0.64	14.3 ± 0.01	15.4 ± 0.64	18.2 ± 0.49	19.7 ± 0.57
56	Caryophyllene oxyde	1578	1572	1.0 ± 0.01	0.6 ± 0.01	1.1 ± 0.01	0.9 ± 0.01	-	-	-	-
57	Dodecyl acetate	1585	1580	0.7 ± 0.14	0.6 ± 0.01	0.6 ± 0.07	0.7 ± 0.07	0.4 ± 0.01	0.5 ± 0.01	0.3 ± 0.01	0.2 ± 0.01
58	α -Cedrol	1603	1596	0.6 ± 0.07	0.3 ± 0.01	0.4 ± 0.01	0.6 ± 0.01	1.9 ± 0.35	1.4 ± 0.01	1.1 ± 0.14	1.4 ± 0.14
59	Hexadecane	1600	1599	0.1 ± 0.01	0.6 ± 0.01	0.3 ± 0.07	0.3 ± 0.01	0.7 ± 0.01	0.5 ± 0.01	0.5 ± 0.01	0.4 ± 0.01
60	Isochavicol 2-methyl Butyrate	1651	1648	3.1 ± 0.21	3.6 ± 0.01	3.4 ± 0.14	2.3 ± 0.21	2.3 ± 0.14	2.3 ± 0.01	2.0 ± 0.07	2.6 ± 0.28
60a	Bisabolol oxide B	1654	1650	0.6 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	0.1 ± 0.01	1.7 ± 0.01	2.5 ± 0.01	1.3 ± 0.01	2.4 ± 0.21

Table 4 Volatile components extracted by HS-SPME from umbels and flowers of *Daucus crinitus* Desf (Continued)

62	Heptadecane	1700	1703	6.0 ± 0.28	1.9 ± 0.28	1.6 ± 0.14	1.7 ± 0.07	7.1 ± 0.35	5.0 ± 0.42	5.1 ± 0.49	4.5 ± 0.57
63	Benzyl benzoate	1730	1723	0.2 ± 0.01	tr	0.1 ± 0.01	0.2 ± 0.07	0.6 ± 0.07	0.5 ± 0.01	0.3 ± 0.01	0.5 ± 0.07
66	Hexadecanal	1782	1787	0.1 ± 0.01	tr	tr	tr	0.1 ± 0.01	tr	tr	tr
67	Neophytadiene	1807	1807	0.1 ± 0.01	tr	0.1 ± 0.01	tr	tr	tr	tr	tr
	% d ^c identification			92,8 ± 0.35	98,8 ± 0.78	94,8 ± 0.64	98 ± 0.64	91,6 ± 0.64	91,2 ± 0.49	94,2 ± 0.85	97,5 ± 0.35
	Total area 10 ⁵ ^e			280,1	247,7	267,9	260,4	524,5	535,7	549,3	558,2
	Hydrocarbon compounds			29,7	21,5	18,8	19,0	30,9	24,7	32,5	29,9
	Oxygenated compounds			63,1	77,3	76,0	79,0	60,7	66,5	61,7	67,6
	Aliphatic compounds			29,0	21,5	20,0	20,2	31,5	27,8	29,2	27,0
	Phenylpropanoid compounds			48,1	64,4	61,6	63,8	48,7	53,4	51,3	56,5
	Hydrocarbon non-terpenic compounds			16,3	9,7	7,2	6,8	23,1	19,1	21,7	19,9
	Hydrocarbon monoterpenes			5,4	3,9	4,1	3,9	2,4	2,0	4,3	5,5
	Hydrocarbon sesquiterpenes			7,9	7,9	7,4	8,3	5,4	3,6	6,5	4,5
	Hydrocarbon diterpenes			0,1	-	0,1	-	-	-	-	-
	Oxygenated non-terpenic compounds			60,8	76,2	74,4	77,2	57,1	62,1	58,8	63,6
	Oxygenated monoterpenes			0,1	0,1	0,2	0,2	-	0,5	0,5	0,2
	Oxygenated sesquiterpenes			2,2	1,0	1,4	1,6	3,6	3,9	2,4	3,8

^a Order of elution is given on apolar column (Rtx-1). Numbers correspond to those in table 1. The compounds that the number is followed by a letter were only identified in HS-fractions.

^b Retention indices of literature on the apolar column (IRI_a) reported from [12-18].

^c Retention indices on the apolar Rtx-1 column (RI_a).

^d Percentages (means of three analyses) obtained by GC-FID (on RTX-1: apolar column) with peak-area normalization under optimized HS-SPME parameters: temperature: 70°C; equilibrium time: 60 min; extraction time: 30 min. Sample locations: Bensekrane (A), Sid Abdeli (B), Terni (C) and Beni Snous (D).

^e Total area is expressed in arbitrary units.

^f The volatile components identified exclusively from the HS-fractions were affected by a letter. Compounds identified from commercial data libraries: National Institute of Standards and Technology, 1999 (1b, 12, 15c, 17a, 19d, 20b); and literature data: König WA, Hochmuth DH, Joulain D, 2001 (3a, 13a, 19b, 19c, 24a, 32b, 35, 36, 36a, 38a, 41, 42).

Regarding the aerial organs, both the leaf and stem volatile fractions were dominated by aliphatic hydrocarbon compounds (22.2%-87.9% and 27.6%-37.9%, respectively) and, in particular, alkanes such as pentadecane **50** (11.9%-16.0% and 19.9%-51.6%, respectively) and heptadecane **62** (9.0%-20.7% and 4.1%-20.7%). In addition, hydrocarbon monoterpenes were identified in stems (28.0%-29.4%), e.g., limonene **9** (7.5%-11.7%) and myrcene **5** (7.4%-10.6%), and isochavicol isobutyrate **53** was identified as a volatile emitted from the leaves (0.2%-19.0%). The occurrence of phenylpropanoids was established from both the volatile fractions emitted from the umbels and flowers (43.1%-88.6%), e.g., isochavicol isobutyrate **53** (26.7%-51.8% and 14.3%-19.7%, respectively) and isochavicol **26a** (7.1%-15.2% and 29.6%-34.7%, respectively). In addition, hydrocarbon aliphatic compounds, in particular pentadecane **50** and heptadecane **62**, were identified and their relative percentage abundance was higher in the volatile fraction extracted from the flowers (the sum was close to 20%) than from the umbels (the sum was close to 10%).

The identification of isochavicol **26a**, a compound not present in our MS libraries, was carried out from a comparison of the retention indices and the EI-MS data with those of laboratory-synthesized compounds obtained from the LAH reduction of isochavicol isobutyrate **53**, and it was confirmed by a comparison with the ¹³C-NMR data reported in the literature [6]. Isochavicol **26a** has been reported to exhibit interesting antiparasitic activity [6], and to the best of our knowledge, this uncommon phenylpropanoid has not been identified in *D. crinitus* before.

The chemical differences observed between both the essential oils and the volatile fractions extracted using HD and SPME, respectively, can be explained by the fact that the first technique is based on the liquid quasi-total extraction of plant volatiles and the latter technique is controlled by a solid/gas equilibrium step. During hydrodistillation, the most volatile compounds and water-soluble compounds are lost in the gaseous phase and in the hydrolate, respectively, whereas, with HS extraction, it is the fiber affinity of each compound that monitors the sampling of the volatiles. As a consequence, it should be noted that 13 aliphatic compounds (**1a-1e**, **3a**, **5b**, **6a**, **15a**, **17c**, **19a**, **22c**, and **24b**) with a low molecular mass and boiling point were identified only in the volatile fractions extracted using HS-SPME. In the same way, isochavicol (**26a**) was absent in the *D. crinitus* essential oil, but its occurrence in the leaf HS fractions as a main component (7.1%-34.7%) can be explained by its solubility in water. Twenty-five compounds (identified by a number followed by a letter in Tables 3 and 4) in total were identified only in the volatile fractions extracted using HS-SPME, and 18

compounds (identified by an asterisk in Table 1) were identified only in the essential oils.

Because the experiments were optimized for the SPME extraction parameters, the extraction temperature was the most important parameter in our plant headspace study. The distribution constants of each component were temperature dependent: the extraction of hydrocarbon monoterpenes and oxygenated sesquiterpenes was improved at a medium temperature (50°C) and at a high temperature (90°C), respectively (Table 2). The optimal temperature (70°C) used for the HS extraction was an analytical compromise based on the maximum amount of volatiles extracted. Regarding the comparison of both techniques in terms of the isolation time, HS-SPME was clearly faster (70 min), whereas 300 min was required for hydrodistillation. In the same way, the amount of plant material used for the headspace analysis was less (1 g), whereas the production of *D. crinitus* oil using hydrodistillation required 200-300 g of plant material. This may be a major reason for the difference in the chemical HS and HD data.

Conclusions

Several conclusions can be drawn concerning the chemistry of *D. crinitus* from this study.

- (i) Two types of essential oil were produced: the root oils, which were mainly composed of aliphatic compounds (87.0%-90.1%); and the aerial part oils, which were mainly composed of phenylpropanoids (43.1%-88.6%).
- (ii) HS-SPME analysis showed a more precise distribution of volatiles in the organs studied: oxygenated aliphatic compounds were well represented in the roots (44.3%-84.0%), hydrocarbon aliphatic compounds in the leaves and stems (31.3%-88.7%), and phenylpropanoids in the flowers and umbels (47.9%-64.2%).
- (iii) Except for two samples, the location of the samples had a minor influence on the plant volatile production.

Finally, this study has demonstrated that HS-SPME extraction can be considered as an alternative technique for isolating volatiles from aromatic plants.

Experimental

Plant Material and Oil Isolation

Samples of each organ (roots, stems, leaves, flowers and umbels) from *D. crinitus* Desf., were collected on November 2008, in Bensekrane (A) [260 m, 35°04'N 1°13'O], Sid Abdelli (B) [258 m, 35°05'N 1°12'O], Terni (C) [1199 m, 34°47'N 1°21'O] and Beni Snous (D) [854 m, 34°37'N 1°34'O] forests near Tlemcen, Algeria.

Voucher specimens were deposited in the herbarium of the Tlemcen University Botanical Laboratory (Voucher number: UBL 05.09). The oils were isolated by hydrodistillation (200 - 300 g of plant per sample) for 6 h using a Clevenger-type apparatus [12] according to the European Pharmacopoeia and yielded 0.02 for roots and 0.03-0.04% for aerial parts.

HS-SPME Conditions

The single organs of *D. crinitus* were cut roughly with scissors (1 - 2 cm long) before subjection to HS-SPME. The SPME device (Supelco) coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS, 30 μm) was used for extraction of the plant volatiles. Optimization of conditions was carried out using fresh aerial parts of the plant (1 g in a 20 mL vial) and based on the number and the sum of total peak areas measured on GC-FID. Temperature, equilibration time and extraction time were selected after nine experiments combining four temperatures (30, 50, 70 and 90°C), four equilibration times (20, 40, 60 and 80 min) and three extraction times (15, 30 and 45 min). After sampling, SPME fibre was inserted into the GC and GC-MS injection ports for desorption of volatile components (5 min), both using the splitless injection mode. Before sampling, each fibre was reconditioned for 5 min in the GC injection port at 260°C. HS-SPME and subsequent analyses were performed in triplicate. The coefficient of variation ($1.9\% < \text{CV} < 19.8\%$) calculated on the basis of total area obtained from the FID-signal for the samples indicated that the HS-SPME method produced reliable results.

Gas Chromatography

GC analyses were carried out using a Perkin Elmer Autosystem GC apparatus (Walton, MA, USA) equipped with a single injector and two flame ionization detectors (FID). The apparatus was used for simultaneous sampling to two fused-silica capillary columns (60 m \times 0.22 mm, film thickness 0.25 μm) with different stationary phases: Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Temperature program: 60 to 230°C at 2°C min^{-1} and then held isothermal 230°C (30 min). Carrier gas: helium (1 mL min^{-1}). Injector and detector temperatures were held at 280°C. Split injection was conducted with a ratio split of 1:80. Injected volume: 0.1 μL . For HS-SPME-GC analysis, only Rtx-1 (polydimethylsiloxane) column was used and volatile components were desorbed in a GC injector with a SPME inlet liner (0.75 mm. I.D., Supelco).

Gas Chromatography-Mass Spectrometry

The oils obtained were investigated using a Perkin Elmer TurboMass Quadrupole Detector, directly coupled to a Perkin Elmer Autosystem XL equipped

with two fused-silica capillary columns (60 m \times 0.22 mm, film thickness 0.25 μm), Rtx-1 (polydimethylsiloxane) and Rtx-Wax (polyethylene glycol). Other GC conditions were the same as described above. Ion source temperature: 150°C; energy ionization: 70 eV; electron ionization mass spectra were acquired with a mass range of 35-350 Da. Oil injected volume: 0.1 μL . The volatile fractions sampling by HS-SPME were analyzed only on a Rtx-1 capillary column and volatile components were desorbed in a GC injector with a SPME inlet liner (0.75 mm. I.D., Supelco).

Component Identification

Identification of the components was based (i) on the comparison of their GC retention indices (RI) on non polar and polar columns, determined relative to the retention time of a series of n-alkanes with linear interpolation, with those of authentic compounds or literature data [13-18]; and (ii) on computer matching with commercial mass spectral libraries [15-19] and comparison of spectra with those of our personal library. Relative amounts of individual components were calculated on the basis of their GC peak areas on the two capillary Rtx-1 and Rtx-Wax columns, without FID response factor correction.

NMR analysis

^{13}C -NMR spectra of the stem oil from Bensekrane station (isochavicol isobutyrate **53**: 84.1 %) were acquired in deuterated chloroform using a Bruker Avance 400 Fourier Transform spectrometer (Wissembourg, France) operating at 100.13 MHz for ^{13}C -NMR and equipped with a 5 mm probe. All shifts were referred to the internal standard tetramethylsilane (TMS). ^{13}C -NMR spectra of the chromatographic fractions were recorded with the following parameters: pulse width, 4 μs (flip angle, 45°); acquisition time, 2.7 s for 128 K Data table with a spectral width of 25,000 Hz (250 ppm); CPD mode decoupling; digital resolution, 0.183 Hz/pt. The number of accumulated scans was 5000 for a sample (around 40 mg of the oil in 0.5 mL of deuteriochloroform) depending of the amount of product. Exponential line broadening multiplication (1 Hz) of the free induction decay was applied before Fourier Transformation.

Reduction of isochavicol isobutyrate **53**

The isochavicol isobutyrate-rich stem oil (200 mg) from Bensekrane, was dissolved in dry Et_2O (4 mL) and was carefully added to a suspension of lithium aluminum hydride (LAH) (100 mg) in dry Et_2O (6 mL) at 0°C. The mixture was stirred at room temperature and then refluxed for 3 h. The reaction mixture was hydrolysed by addition of a solution of NaOH 15 % (2 mL) and cold water. The organic layer was separated, washed

with water to neutrality, dried over Na₂SO₄ and concentrated under vacuum. The mixture (80 mg) exhibited isochavicol (22.3 %) as main components.

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Authors' contributions

MAD collected the plant material. MAD, ND, and JMD performed the HD and HS-SPME extractions, obtained the essential oils and the volatile fractions, and participated in the data analysis. MAD, HA, BT, AM, and JC conceived the study and helped draft the manuscript. HA, BT, AM, and JC performed the coordination of the study, and worked on the data analysis and interpretation. All the authors read and approved the final manuscript.

Competing interests

The authors declare that they have no competing interests.

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