Food Chemistry 112 (2009) 1072–1078

Contents lists available at ScienceDirect

Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

Analytical Methods

Flavour compounds of *Lavandula angustifolia* L. to use in food manufacturing: Comparison of three different extraction methods

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ARTICLE INFO

Article history:
Received 21 February 2008
Received in revised form 19 April 2008
Accepted 8 July 2008

Keywords:
Lavandula angustifolia L.
GC-MS
Supercritical carbon dioxide
Ultrasound extraction
Volatile compounds
Food flavouring

ABSTRACT

Sixty compounds of *Lavandula angustifolia* L. cultivated in Friuli Venezia Giulia (North-East Italy) were identified and quantified by GC-MS and GC-FID from essential oils obtained by means of hydrodistillation, and from extracts obtained by supercritical CO_2 extraction (SFE) and ultrasound-assisted extraction (US). Using absolute calibration, a true quantification of 1-8 cineol, camphor, linalool, linalyl acetate and β-caryophyllene was carried out. The best extracts, in terms of amount of isolated compounds, flavour quality and stability were those obtained with SFE. Sonication performed at low amplitude for 5 min offered respect to high amplitude a promising alternative to hydrodistillation as a source of lavender flavouring ready to use for alcoholic beverages or/and confectionery products.

1. Introduction

The composition of *Lavandula angustifolia* L. essential oil has been extensively investigated (An, Haig, & Hatfield, 2001; Bicchi, Drigo, & Rubiolo, 2000; Chemat, Lucchesi, Smadja, Favretto, Colnaghi, & Visinoni, 2006; Fakhari, Salehi, Heydari, Ebrahimi, & Haddad, 2005; Kim & Lee, 2002; Shellie, Mondello, Marriott, & Dugo, 2002) because of its commercial interest in the fragrance industry (soaps, colognes, perfumes, skin lotion and other cosmetics), in aromatherapy (relaxant), in pharmaceutical preparations for its therapeutic effects as a sedative, spasmolytic, antiviral and antibacterial agent (Kim & Lee, 2002). Recently it has also been employed in food manufacturing as natural flavouring for beverages, ice cream, candy, baked goods and chewing gum.

An essential oil is a volatile mixture of organic compounds derived from odorous plant material by physical means. The constituents of an essential oil may be classified into two principal groups: (a) hydrocarbons (terpenes, sesquiterpenes and diterpenes); (b) oxygenated compounds derived from these hydrocarbons including alcohols, aldehydes, esters, kethons, phenols, oxides, etc. The terpenoid hydrocarbons are characterized by their: (a) poor solubility in dilute alcohol: an essential oil having a high percentage of terpenes is relatively insoluble in dilute alcohol whereas those rich in oxygenated compounds are more readily soluble, and this character is often used as a guide to quality; (b) tendency to oxidize with consequent deterioration in odour and flavour quality: oxidation may be accompanied by polymerization and even resinification; (c) low contribution to the flavour profile: in comparison with the flavour strength of the associated oxygenated compounds their contribution is insignificant (Heath, 1978).

The recovery of an essential oil from plant can be achieved by water distillation (hydrodistillation) or steam distillation (AFNOR T 75-005., 1988). These techniques take at least several hours and require the application of heating, which can cause the degradation of thermo labile compounds present in the starting plant material and therefore an incomplete collection of compounds responsible for its fragrance (Denny, 1988). Due to the harsh conditions prevalent during the distillation process, one expects the odour profile of the fresh raw material to be different than that of the processed oil. These shortcomings lead to the consideration of the use of mild techniques such as supercritical fluid extraction (SFE) using carbon dioxide and ultrasonic-assisted extraction (US).

Supercritical fluid extraction using carbon dioxide gives many benefits for the extraction of products from their natural source (Adasoglu, Dincer, & Bolat, 1994; Herrero, Cifuentes, & Ibanez, 2006; Pallado, Tassinato, D'Alpaos, & Traldi, 1997; Pourmortazavi & Hajimirsadeghi, 2007; Revenchon, Della Porta, & Senatore, 1995). The supercritical fluid extraction processes are performed in the range of temperature in which thermo labile compounds have no thermal stress. As an extraction solvent, CO_2 shows strong lypophilic selectivity; this offers the advantage that extracts are

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doi:10.1016/j.foodchem.2008.07.015

devoid of unwanted compounds (organic and inorganic salts, sugars, amino acids, tannins etc.). Besides, carbon dioxide due to the low critical temperature (31 °C) allows working at mild conditions and its gaseous standard state provides a solvent-free product.

The benefit of using ultrasound in plant extraction has already been demonstrated for bioactive substances (Albu, Joyce, Paniwnyk, Lorimer, & Mason, 2004; Capecka, Mareczek, & Leja, 2005; Surasak, Prasert, & Artiwan, 2006; Vinatoru, Toma, & Mason, 1999), although few application are available concerning the extraction of aroma compounds (Cabredo-Pinillos, Cedron-Fernandez, Gonzalez-Briongos, Puente-Pascual, & Saenz-Barrio, 2006; Caldeira, Pereira, Clımaco, Belchior, & Bruno de Sousa, 2004; Veličković, Milenović, Risti, & Veljković, 2006). The ultrasonic enhancement of extraction is attributed to disruption of cell walls, particle size reduction and enhanced mass transfer of the cell content via cavitation bubble collapse (Romdhane & Gourdan, 2002; Vinatoru et al., 1999).

The aim of this study is to compare different extraction methods of volatile compounds from *L. angustifolia* L. in order to evaluate the most advantageous for food industry application in terms of flavour quality and stability. To investigate the potential of supercritical carbon dioxide extraction and ultrasound extraction, comparisons of aromatic compositions have been made with conventional hydrodistillation for the extraction of fragrances from L. angustifolia L. recently cultivated in Friuli Venezia-Giulia (North-East Italy).

2. Materials and methods

2.1. Plant material

Inflorescence of *L. angustifolia* L. was collected in full bloom in July 2006 during sunny days at different elevations in two parts of Friuli Venezia Giulia (North-East Italy): Low-Friuli (20 m) and High-Friuli (500 m). Each flower sample (only flowers without stems and leaves) analysed was isolated from at least 10 plants and the data reported are the mean of three replicates. The flower samples were not ground because of the superficial position of unicellular glands containing the essential oil. The flowers of *L. angustifolia* L. were identified by Professor Livio Poldini, University of Trieste, Trieste, Italy. A voucher specimen has been deposited at the Herbarium of the University of Trieste (TSB), Trieste, Italy (voucher number 7235).

2.2. Essential oil hydrodistillation

An aliquot of 250 g of lavender flowers was submitted to hydrodistillation (HD) with a Clevenger type apparatus according to the standard procedure described in the European Pharmacopoeia (Council of Europe European (COE) - European Directorate for the Quality of Medicines (EDQM), 2007). The essential oil was co-distilled with water for 3 h, collected, dried under anhydrous sodium sulphate and stored at 0 °C until used. Hydrodistillations were performed at least three times for each sample and the mean values of the extraction yields were reported.

2.3. Supercritical fluid extraction apparatus and procedure

Extractions by supercritical carbon dioxide on lavender flowers were performed on a laboratory extraction unit. In Fig. 1 a schematic diagram of the experimental apparatus used for the extraction with SFE-CO_2 is shown. CO_2 was supplied by a high pressure bomb and was pumped through the plant by an ISCO syringe pump (260D model) working at constant pressure. The cylinder of the pump was maintained at 0 °C by a cooling unit (Haake F3) in order to keep liquid CO_2 during compression. The CO_2 flows first through a heating coil and then through a stainless steel column (l = 20 cm, $Ø_e$ = 1.27 cm) containing the vegetable matrix. This was placed inside a water bath and the temperature kept constant by a Haake DC3 heater (±0.1 °C). The pressure was monitored with a Druck DPI 260 pressure transducer (±0.1%). One separator only was used for the recovery of the extract. The separator was immersed in a cooled bath maintained at −5 °C. A lamination valve (Swagelok SS-31RS4) was located before the separator and allowed the control of the pressure. The valve was heated to prevent clogging and the extract was collected in a separator that can be maintained at temperatures between −10 and 30 °C. The total volume of CO_2 employed during each extraction test was measured with a flow meter Brokhorst S200D (±0.001 l). Supercritical CO_2 extractions tests on lavender flowers were performed in the pressure range from 80 to 120 bar and for temperature between 35 and 60 °C. The best overall performance of the process resulted from the extraction performed at 120 bar of pressure and at a temperature of 40 °C. Optimum conditions were evaluated with respect to the extract composition analysed by GC-MS. The optimum condition was the one at which the minimum amount of higher molecular weight compounds (paraffins) were co-extracted.

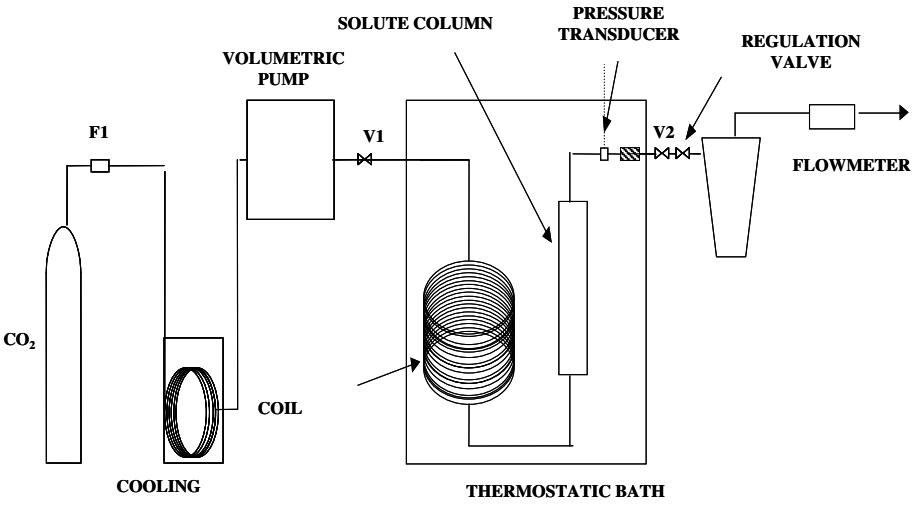

Fig. 1. Schematic representation of the laboratory supercritical fluid extraction apparatus.

Table 1
Chemical composition of *Lavandula angustifolia* essential oils obtained by hydrodistillation (HD)

Compound	Calculated LRI	Ref RI[c]	Ref RI[d]	Sample			
				Low-Friuli		High-Friuli	
				Mean[a] ± CV (%)	Mean[b] ± CV (%)	Mean[a] ± CV (%)	Mean[b] ± CV (%)
α-Thuiene	929	938	930	0.13 ± 2.91		0.11 ± 1.78	
α-Pinene	935	939	935	0.51 ± 2.66		0.93 ± 2.09	
Camphene	950	953	950	0.26 ± 1.63		0.59 ± 1.58	
Thuja-2.4(10)-diene	974		956	0.13 ± 1.37		0.30 ± 1.39	
Sabinene	976	972	976	0.31 ± 1.40		0.75 ± 1.23	
β-Pinene	982	981	978	0.14 ± 0.68		0.30 ± 0.54	
Octen-3-ol	988	982	988	0.22 ± 1.34		0.20 ± 1.47	
3-Octanone	992	999	994	0.36 ± 0.43		0.68 ± 0.56	
Myrcene	996	992	995	0.12 ± 2.24		–	
3-Octanol	1001		1004			0.11 ± 1.08	
α-Phellandrene	1008	1007	1009	0.20 ± 0.27		0.91 ± 0.15	
1.4-Cineole	1016	1018	1023	0.32 ± 0.54		0.11 ± 1.67	
o-Cymene	1022		1026	0.04 ± 0.95		0.09 ± 1.03	
p-Cymene	1024	1027	1028	0.29 ± 0.62		0.20 ± 0.47	
Limonene	1029	1030	1031	1.10 ± 0.33		2.36 ± 0.14	
1,8-Cineole	1031	1030	1036	3.98 ± 2.31	0.07 ± 0.75	10.89 ± 0.48	0.22 ± 0.58
(Z)-β-Ocimene	1041	1043	1043	1.02 ± 0.35		1.32 ± 0.37	
(E)-β-Ocimene	1051	1052	1053	1.24 ± 0.25		0.42 ± 0.45	
γ-Terpinene	1060		1062	–		0.12 ± 1.78	
cis-Sabinene hydrate	1068	1073	1075	0.39 ± 0.32		0.34 ± 0.38	
cis-Linalool oxide	1074		1079	0.09 ± 9.65		0.07 ± 8.92	
trans-Linalool oxide	1086		1088	–		0.07 ± 5.68	
Terpinolene	1088	1090	1088	0.10 ± 0.20		0.39 ± 0.19	
Perillene	1097	1126	1102	0.16 ± 9.11		0.05 ± 7.89	
Linalool	1100	1100	1112	35.96 ± 0.54	0.62 ± 0.60	36.51 ± 0.62	0.74 ± 0.46
Octen-1-ol-acetate	1106			0.06 ± 5.67		–	
Endo-fenchol	1113	1139	1114	0.46 ± 6.83		–	
Camphor	1145	1139	1152	5.56 ± 0.35	0.10 ± 0.45	11.76 ± 0.76	0.24 ± 0.28
trans-Pinocarveol	1151	1169	1146	0.18 ± 1.05		0.10 ± 0.97	
Borneol	1167	1162	1172	2.71 ± 0.68		4.21 ± 1.24	
Lavandulol	1175	1186	1175	0.05 ± 1.20		0.05 ± 1.32	
Terpinen-4-ol	1178	1179	1184	6.57 ± 4.65		2.10 ± 3.79	
m-Cymen-8-ol	1185		1187	0.03 ± 4.77		0.09 ± 6.78	
p-Cymen-8-ol	1190		1190	0.33 ± 7.04		0.55 ± 8.04	
Neoisomenthol	1192		1193	1.31 ± 6.98		0.47 ± 7.00	
α-Terpineol	1196	1195	1198	0.06 ± 2.31		0.07 ± 1.96	
cis-Carveol	1229	1229	1228	0.11 ± 7.06		0.11 ± 8.55	
Hexyl-2-methyl butyrate	1239	1239	1243	0.30 ± 3.92		0.23 ± 3.27	
Isobornyl formate	1244	1245	1237	0.06 ± 1.58		0.10 ± 2.05	
Linalyl acetate	1258	1261	1264	21.74 ± 1.16	0.38 ± 0.23	14.42 ± 2.02	0.29 ± 0.37
Dihydro linalool acetate	1287		1286	0.05 ± 3.10		–	
Lavandulyl acetate	1291		1298	2.42 ± 5.84		0.19 ± 5.41	
Terpineol acetate	1332			0.20 ± 1.38		0.13 ± 2.01	
Neryl acetate	1366	1362	1371	0.06 ± 4.22		–	
Geranyl acetate	1383	1382	1390	0.10 ± 1.63		0.20 ± 1.78	
Daucene	1387		1384	0.28 ± 2.89		0.16 ± 3.07	
β-Bourbonene	1392	1417	1394	0.17 ± 3.45		0.09 ± 2.91	
α-*cis*-Bergamotene	1418		1420	0.07 ± 2.65		0.06 ± 1.94	
(E)-Caryophyllene	1424	1438	1426	2.87 ± 6.32	0.05 ± 0.21	2.42 ± 6.12	0.05 ± 0.32
Lavandulyl isobutyrate	1439		1435	0.22 ± 1.56		0.06 ± 2.56	
α-*trans*-Bergamotene	1446	1431	1440	0.07 ± 2.53		0.05 ± 2.34	
β-Farnesene	1459	1445	1461	4.02 ± 2.73		1.07 ± 1.05	
γ-Muurolene	1474	1475		0.06 ± 3.42		0.15 ± 3.16	
Germacrene D	1485	1487	1464	0.77 ± 1.98		1.50 ± 0.98	
(−)-β-Bisabolene	1500	1498		0.03 ± 3.53		–	
Lavandulyl isovalerate	1502		1504	0.07 ± 2.09		0.12 ± 2.18	
trans γ-Cadinene	1509		1515	0.26 ± 2.64		0.39 ± 2.12	
δ-Cadinene	1518	1519	1522	0.13 ± 2.62		0.06 ± 3.04	
Spathulenol	1589	1619	1586	0.06 ± 2.61		0.31 ± 1.89	
α-Muurolol	1646		1652	0.23 ± 3.02		0.06 ± 3.34	
α-Bisabolol	1697	1662	1698	1.12 ± 3.98		0.89 ± 2.05	
Monoterpene hydrocarbons				5.59		7.78	
Oxygenated monoterpenes				83.20		82.62	
Sesquiterpene hydrocarbons				3.46		2.73	
Oxygenated sesquiterpene				6.69		4.43	
Yield (%)				0.5 ± 1.89		1.02 ± 1.77	

[a] GC peak area percentage.
[b] mg for g of the starting flowers.
[c] http://www.flavournet.org.
[d] Shellie et al. (2002) a results expressed as mean of three replications ± coefficient of variation (%).

An aliquot of 1 g of dried matter, not grounded, was used for each run. The extraction was performed at 120 bar of pressure and at temperature of 40 °C for 120 min with a flow rate of 27 l h^{-1}.

Extractions were performed at least three times for each sample and the mean values of the extraction yields were reported. The yield of extraction was calculated from the initially mass of the plant material in the extractor and the mass of the extract.

2.4. Ultrasound apparatus and procedure

Sonochemical experiments were carried out using an ultrasonic probe (Elettrofor Sonoplus model HD2200 with TT13FZ probe, Bandelin, Berlin; 20 KHz working frequency; 200 W – amplitude setting displayed in % on the scale of 10–100). The probe was operated at 25 (US 25) and 100% (US100) of the scale. An aliquot of 10 g of lavender flowers was added with 100 ml of 70% ethanol v/v (extracting solvent) in a 250 ml conical flask and the probe was submerged about 2–5 mm under the surface of the mixture. The choice of ethanol–water solution as extracting solvent was made based on its polarity relative to the aroma compounds of lavender and its acceptability for practical use. A stirrer was used to obtain good solvent/plant material contact. The maximum reached temperature at the end of each sonication was lower than 60 °C. The mixture was sonicated for 5 min. The liquid extract was separated from the residual plant material by filtration and concentrated under vacuum at 50 °C in a rotary evaporator. The GC analysis of the aroma volatile compounds of lavender flowers was carried out on the distilled solvent. It was extracted three times with 5 ml of *n*-hexane and concentrated under a nitrogen stream to 1 ml. The mass of each concentrate was determined using an analytical balance after the complete evaporation of *n*-hexane. Extractions and consequently solvent distillations were performed at least three times for each sample and the mean values of the yields were reported. The yield of extraction was calculated from the initially mass of the plant material and the mass of the concentrate.

2.5. GC-MS and GC-FID analyses

The essential oils and extracts compositions were determined by GC. GC-MS analysis was performed using a Varian 3400 gas chromatograph coupled to a Varian Saturn ion trap detector was. The fused-silica column was a DB-5 fused-silica column (Supelco, Bellafonte, PA) (30 m × 0.25 mm i.d., film thickness 0.25 μm). GC-MS data were obtained using the following conditions: carrier gas helium (He 99.9995%); flow rate 2.0 ml min^{-1}; the split ratio 1/70 (v/v). An aliquot of 100 mg of distilled oils were diluted with 1 ml *n*-hexane, as were the extracts, and 1.0 μl was injected into the GC-MS system. The oven temperature program was: 45 °C for 3 min, from 45 to 250 °C at 3 °C min^{-1}, and holding 250 °C for 5 min. The injector, transfer line and ion trap temperatures were, respectively, 250, 280 and 200 °C. The electron impact (70 eV) spectra were recorded at 1 s/scan with a filament emission current of 10 μA. The identification of volatile compounds was based both on comparison of the linear retention indexes, RI calculated using the Van der Dool and Kratz's equation with those reported by literature (Shellie et al., 2002; http://www.flavournet.org) and on the matching of mass spectra of the compounds with the reference mass spectra of two libraries (Wiley5 and Nist90) coupled with the software of GC-MS and Adams' library (Adams, 1995). For the major chromatographic peaks, identification was also confirmed using authentic standards (1,8-cineol, linalool, camphor and linaly acetate) (Sigma Aldrich, Milan, Italy).

A Carlo Erba 8000 Top series gas chromatograph (CE Instruments, Milan, Italy) equipped with a flame ionization detector and split–splitless injector was used for quantitative analysis. The same column and the same operation conditions applied in GC-MS analysis were used. Quantitative analysis of 1-8 cineol, camphor, linalool, linalyl acetate and β-caryophyllene (99.0–99.5% purity purchased from Sigma Aldrich (Milan, Italy) was performed by absolute calibration. The detector response was found to be linear, with an R^2 value of 0.99, over a range of 0-10 mg ml^{-1} for 1-8 cineol; 0–25 mg ml^{-1} for linalool; 0–20 mg ml^{-1} for linalyl acetate; 0–15 mg ml^{-1} for camphor and 0–2.5 mg ml^{-1} for β-caryophyllene. The concentration of the major volatile compounds of lavender were expressed as mg for g of the starting flowers.

3. Results and discussion

3.1. Composition of essential oils (HD)

The identified components from lavender essential oils, their retention indices, their percentage composition and the concentration of the most significant compounds (Tucker, Maciarello, & Howell, 1984) have been summarized in Table 1. Quantitative

Table 2
Chemical composition of *Lavandula angustifolia* extracts obtained by supercritical CO_2 extraction (SFE)

Compound	Sample			
	Low-Friuli		High-Friuli	
	Mean[a] ± CV (%)	Mean[b] ± CV (%)	Mean[a] ± CV (%)	Mean[b] ± CV (%)
1,8-Cineol	–	–	0.67 ± 0.29	0.30 ± 0.76
Linalool	45.78 ± 0.23	1.92 ± 0.42	43.30 ± 0.50	1.79 ± 0.61
Camphor	7.02 ± 0.37	0.29 ± 0.52	8.20 ± 0.42	0.34 ± 0.62
Borneol	6.77 ± 0.57	–	3.66 ± 0.48	–
Terpinen-4-ol	4.45 ± 4.38	–	–	–
Linalyl acetate	17.91 ± 1.20	0.75 ± 0.26	21.00 ± 1.18	0.87 ± 0.23
Bornyl acetate	–	–	2.88 ± 1.57	–
(E)-Caryophyllene	3.04 ± 5.18	0.12 ± 0.32	3.96 ± 6.12	0.16 ± 0.31
β-Farnesene	3.52 ± 2.84		2.15 ± 2.70	
Germacrene D	1.59 ± 2.04		–	
α-Muurolol	2.45 ± 3.26		–	
α-Bisabolol	6.75 ± 3.98		11.87 ± 2.89	
Oxygenated monoterpenes	74.91		71.51	
Sesquiterpene hydrocarbons	3.04		3.96	
Oxygenated sesquiterpene	14.32		16.33	
Yield (%)	3.2 ± 3.48		3.7 ± 4.53	

Results expressed as mean of three replications ± coefficient of variation (%).
[a] GC peak area percentage.
[b] mg for g of the starting flowers.

but not qualitative differences were found in the chemical composition of both analysed essential oils, depending on the localisation of the cultivation area. Linalool (35.96–36.51%) (0.62–0.74 mg g^{-1}) and linalyl acetate (21.74–14.42%) (0.38–0.29 mg g^{-1}) were found as the principal components in both essential oils. The amount of 1,8-cineole (3.98–10.89%) (0.07–0.22 mg g^{-1}) and camphor (5.56–11.76%) (0.10–0.24 mg g^{-1}) varied moderately. The samples fitted closest to the acceptable ranges for the major components of *L. angustifolia* essential oil stated in the ISO Standard 3515 for linalool, linalyl acetate, 1,8-cineole but had higher percentages of camphor. The yields obtained by means of HD, which is one the reference method in essential oil extraction, were 0.5–1.02%.

Table 3
Chemical composition of *Lavandula angustifolia* extracts obtained by sonication at different ultrasonic power (US)

Compound	Sample							
	Low-Friuli				High-Friuli			
	US25		US100		US25		US100	
	Mean[a] ± CV (%)	Mean[b] ± CV (%)	Mean[a] ± CV (%)	Mean[b] ± CV (%)	Mean[a] ± CV (%)	Mean[b] ± CV(%)	Mean[a] ± CV (%)	Mean[b] ± CV (%)
α-Thuiene	0.03 ± 1.85		0.10 ± 2.05		0.04 ± 1.43		0.04 ± 1.68	
α-Pinene	0.22 ± 1.28		0.66 ± 1.47				0.31 ± 1.56	
Camphene	0.18 ± 0.77		0.50 ± 0.21		0.27 ± 0.53		0.26 ± 0.14	
Thuja-2,4(10)-diene	0.16 ± 0.62		0.25 ± 0.96		0.17 ± 1.10		0.15 ± 0.72	
Sabinene	0.38 ± 1.09		0.60 ± 0.89		0.40 ± 1.24		0.35 ± 0.63	
β-Pinene	0.12 ± 0.35		0.15 ± 0.67		0.12 ± 0.75		0.16 ± 1.03	
Octen-3-ol	0.17 ± 1.11		0.49 ± 1.32		0.35 ± 0.89		0.29 ± 1.18	
3-Octanone	0.48 ± 0.42		0.69 ± 0.48		0.53 ± 0.72		0.41 ± 0.50	
Myrcene	0.06 ± 1.53		0.10 ± 1.81		0.06 ± 1.04		0.05 ± 1.49	
3-Octanol	0.06 ± 0.94		0.10 ± 1.14		0.07 ± 1.43		0.07 ± 1.33	
α-Phellandrene	0.10 ± 0.46		0.41 ± 0.66		0.41 ± 0.32		0.40 ± 0.47	
1,4-Cineole	0.17 ± 0.39		0.23 ± 0.95		0.09 ± 0.68		0.05 ± 0.62	
o-Cymene	–		–		0.01 ± 0.97		–	
p-Cymene	0.07 ± 0.40		0.23 ± 0.21		0.13 ± 0.83		0.04 ± 0.46	
Limonene	0.78 ± 0.29		2.11 ± 0.41		1.45 ± 0.44		0.11 ± 0.81	
1,8-Cineole	11.17±0.23	0.26 ± 0.53	14.24 ± 0.65	0.25 ± 0.22	12.84 ± 0.36	0.41 ± 0.62	13.41 ± 0.60	0.35 ± 0.99
(Z)-β-Ocimene	0.55 ± 0.47		1.36 ± 0.38		1.12 ± 0.82		1.00 ± 0.57	
(E)-β-Ocimene	0.19 ± 0.21		0.47 ± 0.53		0.36 ± 0.53		0.28 ± 1.03	
γ-Terpinene	–		–		0.09 ± 0.60		0.06 ± 0.83	
cis-Sabinene hydrate	0.35 ± 0.18		0.32 ± 0.20		0.25 ± 0.34		0.32 ± 0.95	
cis-Linalool oxide	0.10 ± 4.34		0.17 ± 5.81		0.04 ± 6.01		0.14 ± 4.77	
Terpinolene	0.46 ± 0.06		0.59 ± 0.25		0.43 ± 0.13		0.38 ± 0.34	
Linalool	27.88 ± 0.31	0.64 ± 0.88	32.78 ± 0.84	0.62 ± 0.97	31.23 ± 0.48	1.17 ± 0.81	37.37 ± 0.55	0.89 ± 0.68
Octen-1-ol-acetate	–		–		0.09 ± 0.57		0.08 ± 0.16	
Endo-fenchol	0.21 ± 2.98		0.17 ± 3.28		–		–	
Camphor	10.05±0.11	0.24 ± 0.49	12.61 ± 0.33	0.24 ± 0.77	11.86 ± 0.41	0.40 ± 0.54	13.64 ± 0.12	0.29 ± 0.18
trans-Pinocarveol	0.19 ± 0.57		0.27 ± 0.39		0.25 ± 0.49		0.19 ± 0.82	
Borneol	1.48 ± 0.24		1.86 ± 0.56		1.99 ± 0.76		3.17 ± 0.60	
Lavandulol	–		–		0.11 ± 0.77		0.06 ± 1.19	
Terpinen-4-ol	3.34 ± 2.14		3.32 ± 1.74		2.30 ± 0.74		2.49 ± 0.24	
p-Cymen-8-ol	0.67 ± 5.63		1.23 ± 4.91		0.22 ± 4.23		0.35 ± 5.35	
Neoisomenthol	–		–		1.00 ± 5.92		0.68 ± 4.98	
cis-Carveol	0.01 ± 4.50		–		0.08 ± 3.63		0.08 ± 4.39	
Hexyl-2-methyl butyrate	0.19 ± 2.89		0.43 ± 3.04		0.42 ± 2.54		0.30 ± 3.74	
Isobornyl formate	0.18 ± 0.71		0.14 ± 1.11		0.19 ± 0.85		0.16 ± 0.71	
Linalyl acetate	34.66 ± 1.20	0.85 ± 0.31	18.07 ± 1.76	0.29 ± 0.45	20.64 ± 1.30	0.75 ± 0.49	16.32 ± 1.97	0.59 ± 0.82
Lavandulyl acetate	0.37 ± 3.33		0.42 ± 2.83		0.20 ± 0.89		0.13 ± 1.89	
Terpineol acetate	0.13 ± 1.02		0.16 ± 1.29		0.22 ± 1.98		0.14 ± 0.87	
Geranyl acetate	–		–		0.24 ± 1.30		0.15 ± 0.79	
Daucene	0.24 ± 0.76		0.22 ± 0.65		0.23 ± 0.15		0.16 ± 0.21	
β-Bourbonene	0.10 ± 0.58		0.12 ± 0.89	–	–			
α-*cis*-Bergamotene	0.01 ± 1.43		–		0.06 ± 2.64		0.11 ± 3.17	
(E)-Caryophyllene	2.97 ± 4.17	0.07 ± 0.62	2.50 ± 3.96	0.05 ± 0.94	3.14 ± 4.32	0.11 ± 0.87	2.36 ± 3.46	0.08 ± 0.26
Lavandulyl isobutyrate	–		–		0.25 ± 1.57		0.18 ± 0.42	
β-Farnesene	1.06 ± 1.59		1.38 ± 2.12		1.61 ± 1.28		1.06 ± 2.37	
γ-Muurolene	0.15 ± 2.30		0.11 ± 2.90		0.16 ± 3.04		0.12 ± 3.64	
Germacrene D	1.16 ± 0.71		1.36 ± 0.79		2.37 ± 0.95		1.54 ± 1.11	
Lavandulyl isovalerate	0.06 ± 1.32		0.06 ± 1.04		0.11 ± 1.49		0.01 ± 1.01	
trans γ-Cadinene	–		–		0.47 ± 2.13		0.25 ± 1.26	
δ-Cadinene	–		–		–		–	
Spathulenol	–		–		0.29 ± 2.26		0.12 ± 1.58	
α-Muurolol	–		–					
α-Bisabolol	–		–		0.64 ± 4.52		0.42 ± 5.20	
Monoterpene hydrocarbons	3.31		7.53		4.95		3.52	
Oxygenated monoterpenes	90.82		86.07		84.17		89.09	
Sesquiterpene hydrocarbons	3.32		2.84		3.43		2.63	
Oxygenated sesquiterpene	2.38		2.85		5.55		3.51	
Yield (%)	0.21 ± 5.32		0.18 ± 6.25		0.35 ± 4.39		0.26 ± 6.87	

Results expressed as mean of three replications ± coefficient of variation (%).
[a] GC peak area percentage.
[b] mg for g of the starting flowers.

Table 4
Concentration of the major volatile compounds (mg g^{-1}) s of *Lavandula angustifolia* in essential oils (HD) and extracts obtained by sonication at different ultrasonic power (US)

Compound (mg g^{-1})	Sample low-Friuli			High-Friuli		
	HD	US25	US100	HD	US25	US100
1,8-Cineol	0.07 ± 0.75	0.26 ± 0.53	0.25 ± 0.22	0.22 ± 0.58	0.41 ± 0.62	0.35 ± 0.99
Linalool	0.62 ± 0.60	0.64 ± 0.88	0.62 ± 0.97	0.74 ± 0.46	1.17 ± 0.81	0.89 ± 0.68
Camphor	0.10 ± 0.45	0.24 ± 0.49	0.24 ± 0.77	0.24 ± 0.28	0.40 ± 0.54	0.29 ± 0.18
Linalyl acetate	0.38 ± 0.23	0.85 ± 0.31	0.29 ± 0.45	0.29 ± 0.37	0.75 ± 0.49	0.59 ± 0.82
(E)-Caryophyllene	0.05 ± 0.21	0.07 ± 0.62	0.05 ± 0.94	0.05 ± 0.32	0.11 ± 0.87	0.08 ± 0.26

Results expressed as mean of three replications ± coefficient of variation (%).

3.2. Composition of extracts obtained by supercritical–CO_2 extraction (SFE)

Table 2 reports the composition of lavender extracts obtained by supercritical carbon dioxide. Unlike the essential oils, hydrocarbon monoterpenes do not contribute to SFE CO_2 extracts composition and oxygenated sesquiterpenes appeared in higher content. This should be advantageous for the flavour quality of the SFE extracts as the terpenoid hydrocarbons have been characterized by a tendency to oxidize with consequent deterioration in odour and oxygenated compounds make the product valuable (Heath, 1978). In the supercritical extracts the concentrations of linalool, camphor, linalyl acetate and (E)-caryophyllene resulted higher than in the hydrodistilled oils (Table 2). This confirms that the quality of the SFE extracts was better than essential oils because the starting composition of the vegetable matter has been preserved. An extraction time of 120 min with SFE provided higher yields (3.20–3.70%) than those obtained after 180 min by mean of HD (0.5–1.02%).

3.3. Composition of extracts obtained by sonication at different ultrasonic power (US)

Composition of volatile extracts obtained by the distilled solvents obtained from the ultrasound extraction are shown in Table 3. The concentration of the major volatiles and the yields of extraction decreased with increasing ultrasonic power from 25% to 100%. An explanation for this might be that the larger the amplitude of ultrasound wave travelling through a mass medium, the more violently the bubble collapse. Since the collapse of cavitation bubbles generates transient hot spots with extremely high local temperature and pressure (Tuulmets & Salmar, 2001), when the applied ultrasonic power is higher it results in a degradation of thermo labile compounds responsible for the fragrance. Comparing the effect of hydrodistillation and ultrasound irradiation at 25% and 100% on the quantified volatile compounds (Table 4), both the samples treated at ultrasonic power at 100% present concentrations of volatile very close with those obtain by hydrodistillation.

4. Conclusions

The results show both quantitative and qualitative differences among the extracts. The most rich extracts, in terms of amount of isolated compounds, were those obtained with SFE. Likewise, significantly more sesquiterpenes were quantified in the supercritical fluid extracts than those obtained with the other extraction techniques tested. Besides, the opposite has been found for the amount of monoterpene hydrocarbons and this should be advantageous in term of food flavouring stability and quality since essential oils, due to terpenoid hydrocarbons, undergo changes with consequent deterioration in odour and flavour quality. The distilled ethanol–water solution obtained from the ultrasound extractions carries out at low ultrasonic power offered a promising alternative to hydrodistillation as a source of lavender flavouring ready to use for alcoholic beverages or/and confectionery products.

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