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# Comparison of Different Extraction Methods for the Determination of Essential oils and Related Compounds from Coriander (*Coriandrum sativum* L.)

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## Abstract

The volatile oil of coriander (*Coriandrum sativum* L.) obtained from the fruits by soxhlet-dynamic headspace (S-DHS), solvent extraction (SE), steam distillation (SD), hydrodistillation (HYD) and supercritical CO<sub>2</sub> extraction (SC-CO<sub>2</sub>) were analyzed by GC-FID and GC-MS. The SC-CO<sub>2</sub> offered a higher yield (4.5%, w/w) than the other used techniques. Among the identified constituents, linalool was the main compound whatever the employed extraction procedure in contrast to the remaining components which varied according to the isolation technique showing a strong effect of the method used on the composition of these minor compounds. SC-CO<sub>2</sub> as compared to the other extraction techniques revealed its high efficiency in addition to the integrity saving of coriander fruit volatiles. Statistical analysis showed that all the detected and identified compounds were highly ( $P > 0.001$ ) affected by the extraction technique used except the  $\alpha$ -terpineol which appear stable. On the other hand, principal component analysis (PCA) revealed on the determination of one group represented by SC-CO<sub>2</sub>, S-DHS and HYD suggesting a similar essential oil composition. Obtained results show that, in Tunisian coriander essential oil, linalool was the main compound.

**Keywords:** Coriander, Apiaceae, Fruit, Extraction methods, Essential oil composition, Linalool

## 1. Introduction

Nowadays, the identification of organic compounds from the extracts of plants is of great importance, mainly because they can be used as an excellent source of pharmaceutical products for phytotherapy. Since plant extracts are complex mixtures of organic compounds, they request appropriate fractionation techniques to allow a better analysis of their individual constituents. Coriander (*Coriandrum sativum* L.) is an important cash crop of Tunisia. It is also extensively grown in Russia, Central Europe, Asia and Morocco. The stem, leaves and fruits have a

pleasant aroma. The young plant (green coriander) is used in preparing sauces and flavouring curries and soups. The fruits are extensively used as a condiment. In the USA and Europe, coriander is also used for flavouring liquors. The aroma and flavour of coriander fruits are due to the essential oil present in oil glands in the mericarp. The essential oil is also employed in medicine as a carminative or as flavouring agent to cover the bitter taste of other medicines. Powdered fruits or dry extract, tea, tincture, decoction or infusion have been recommended for dyspeptic complaints, loss of appetite, convulsion, insomnia and anxiety.<sup>1</sup> Moreover, the essential oils and various extracts

from coriander have been shown to possess antibacterial,<sup>2</sup> antioxidant,<sup>3</sup> antidiabetic<sup>4</sup> and anticancerous and antimutagenic<sup>5</sup> activities. Evaluations of the oil composition extracted from leaves, flowers, stems and roots have also been reported.<sup>6</sup>

Depending on the extraction method used, the volatile oil composition may change leading to deviations from the natural odour of the plant.<sup>7,8</sup> Hydrodistillation (HYD) and steam distillation (SD) are the traditional methods to isolate essential oils from aromatic plants, although these two methods present some problems, namely, hydrolysis and thermal degradation. To overcome these limitations, an alternative method, supercritical fluid extraction (SFE), has been applied.<sup>9,10</sup> Supercritical fluids provide a higher solubility of the components of the volatile oil, as well as improved mass-transfer rates. Moreover, the manipulation of parameters as temperature and pressure leads to the extraction of different components, which can be useful when a particular component is required.<sup>7,8,10,11,12,13</sup> Since, the supercritical CO<sub>2</sub> method extracted oil presenting a flavour resembling the original material. The development of industrial applications has been carried out.<sup>14</sup> Recently, a published review indicates that the number of independent patents in the area had reached 8600.<sup>15</sup>

The aim of this work was to study the influence of the various process parameters as pressure, particle size and CO<sub>2</sub> flow rate on the extraction yield and composition of the volatile oil from Tunisian coriander fruits, comparing the extracts with those obtained by hydrodistillation (HYD), steam distillation (SD), solvent extraction (SE) and soxhlet-dynamic headspace (S-DHS). The evolution of the extraction was also studied and the samples collected during the process were analyzed to understand how they influence the final composition of the volatile oils.

## 2. Materials and Methods

### 2.1. Materials

Coriander fruits at full ripeness stage were harvested randomly by hand from plants cultivated in the region of Menzel Temime (North-Eastern Tunisia; latitude 36°46'17.80''(N); longitude 10°46'03.38''(E), altitude 141.43 m) during June 2004. Menzel Temime region is characterized by low annual rainfall of 700 mm and mean annual temperature of 16.8 °C. Samples of the fruits were dried in an oven at 60 °C until they reached a constant weight (after 4 days).

### 2.2. Methods

#### 2.2.1. Steam Distillation (SD)

100g of ground coriander fruits was used for each extraction for 3 hours. The procedure basically consists in the passage of the vapor generated in a boiler by the bed

where the plants were put on. Then, the solute was dragged and after that it was condensed by contact with cold water. Due to the difference of density between the oil and the water, the phases separate. The experiments were performed in triplicate. The experimental data of essential oil volume extracted through steam distillation is weighted in order to determine the essential oil yield.

#### 2.2.2. Soxhlet-dynamic Headspace (S-DHS)

Three samples of coriander fruits were finely ground in an electric grinder (IKA-WERK. Type: A: 10). Fifty grams of each ground material was extracted in a soxhlet-extractor with 100 mL hexane (Analytical Reagent, LabScan, Ltd, Dublin, Ireland) for 6 h. The extraction was protected from light. The extract was then filtered and evaporated in a rotary-evaporator under a reduced pressure and temperature. Thirty millilitres of the concentrated solvent extract were subjected to a modified dynamic headspace technique. Thus, the solvent extract sample was introduced into Pyrex tube (25 mm × 400 mm), heated at 40 °C in a water bath, stripped for 3 hours with purified N<sub>2</sub> (1.2 dm<sup>3</sup>/min) and trapped on 50 mg of activated charcoal (particle size 75% ≤ 40 μm, Switzerland) used as adsorbent agent. Yield of this procedure was calculated as the difference between the mass of saturated charcoal and the neutral one. The desorption step was achieved by adding 1 mL of n-pentane to the aforementioned adsorbant and an aliquot of 1 μL was immediately analyzed.

#### 2.2.3. Solvent Extraction (SE)

After a short optimization of several parameters, namely, amount of plant material, extraction time, and solvent used (e.g., n-pentane, n-hexane, n-heptane and 2-methyl-butane), 10 g of dried plant material was extracted in triplicate by a 50 mL of 2-methyl-butane (Analytical Reagent, LabScan, Ltd., Dublin, Ireland) at room temperature during 30 min.<sup>16</sup> After centrifugation at 3000 × g for 10 min, the organic layer was then concentrated at 27.9 °C using a Vigreux column at atmospheric pressure and the concentrated extract was subsequently analyzed.

#### 2.2.4. Supercritical CO<sub>2</sub> Extraction (SC-CO<sub>2</sub>)

A single pass flow apparatus similar, in principle, to that of Stahl and Gerard<sup>17</sup> was used for the essential oil extraction from coriander fruit in compressed carbon dioxide. Figure 1 shows a schematic diagram of this apparatus. Carbon dioxide from the gas cylinder is compressed by reciprocating diaphragm compressor (Nova Swiss) to the operating pressure and flows through a first cell (200 cm<sup>3</sup>) which damps compressor pulsation and partially acts as preheater. From the damper the gas flows slowly into the saturator which is composed of two identical stainless-steel cylinders connected by a short high pres-

sure tube. Each cylinder is 80 mm long with an internal volume of about 100 cm<sup>3</sup>. The lower cell is filled with inert packing material, while the upper one is filled with the desired solute. In order to prevent foam formation, thirty g of activated charcoal (particle size 75% ≤ 40 μm, Switzerland) were coated with solute (about 20g) and put in the saturator, instead of liquid solute. About 75% of the upper cylinder of the saturator is filled with the solute coated spherical particle while the remaining 25% upper part is filled with glass-wool. The carbon dioxide-solute mixture leaving the top of the saturator is expanded to the atmospheric pressure through the micrometering valve V<sub>2</sub> into cold glass traps where the solute condenses. The mass flow rate of the solvent gas is continuously monitored by a mass flow meter (Micro Motion) which also acts as totalizer with an accuracy of ± 0.4% of the rate ± zero stability. Two porous steel filter/distributors are located at the bottom and the top of the upper cylinder while one filter/distributor is located at the top of the lower cylinder of the saturator. The whole saturator is kept at constant temperature by means of an aluminum mantle through which the thermostating fluid flows. The pressure is measured by a pressure transducer (Haenni EDR 430) located at the top of the saturator with an accuracy of 0.15% and it is displayed by an indicator. The temperature is measured, with an accuracy of ± 0.2 °C, by a J thermocouple, located inside the saturator as shown in Figure 1. Both micrometering valves V1 and V2 are used to adjust the pressure and flow rate at the desired valves. At the end of each run, all the collected solute is recovered from the glass traps using ethanol as solvent. The resulting liquid solution is then analyzed on a gas chromatograph equipped with a flame ionization detector (FID) detector. To start with, the saturator is thermostated to the desired temperature and is then pressurized very slowly to the desired pressure. After reaching the desired temperature and pressure values, the saturator is left in this state for about 12 hours. A series of isothermal experimental data

is obtained ranging from lower pressures to higher ones. The total carbon dioxide flow is varied depending on the operating pressure: at lower pressures where the solute solubility is small, a constant mass flow rate of about 0.5 g/min is maintained for a time of about 5 hours, while at higher pressures, owing to the greater amount of solute extracted, the time is reduced to less than 1 hour with the same mass flow rate of carbon dioxide. The apparatus and the procedure described above were previously tested by measuring the solubility of water in compressed carbon dioxide 348.2 K and at pressures of 150 and 200 bar.

## 2. 2. 5. Hydrodistillation (HYD)

The essential oil was isolated from the dried coriander fruit (100 g) by conventional HYD for 3 h according to the European Pharmacopoeia method.<sup>18</sup> The distillate (100 mL) was extracted with 100 mL of 2-methyl-butane (Analytical Reagent, LabScan, Ltd., Dublin, Ireland) for 30 min (three times) and dried over anhydrous sodium sulphate. The organic layer was then concentrated at 27.9 °C using a Vigreux column at atmospheric pressure and the resulting essential oil was weighted for essential oil yield determination and re-diluted for subsequent analyses.

## 2. 2. 6. Gas chromatography (GC-FID) analysis

Analysis of essential oil volatile compounds by gas chromatography (GC) was carried out on a Hewlett-Packard 6890 gas chromatograph (Palo Alto, CA, USA) equipped with a flame ionization detector (FID) and an electronic pressure control (EPC) injector. A polar HP Innowax (PEG) column and an apolar HP-5 column (30 m × 0.25 mm, 0.25 μm film thickness; Hewlett-Packard, CA, USA) were used. The flow of the carrier gas (N<sub>2</sub>) was 1.6 mL/min. The split ratio was 60:1. The analysis was performed using the following temperature program: oven

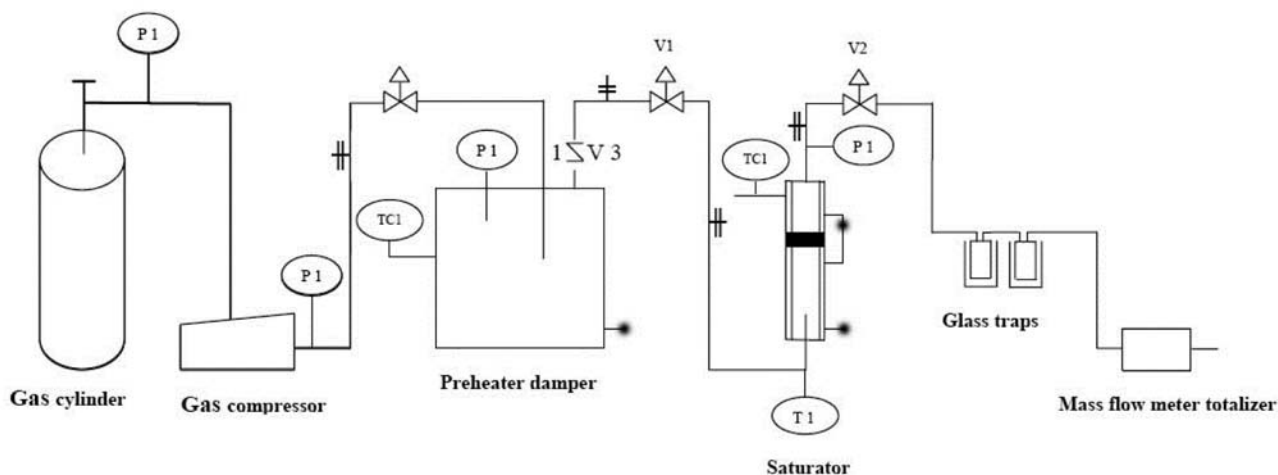


Figure 1: Schematic diagram of the single pass flow experimental apparatus

temperature kept isothermally at 35 °C for 10 min, increased from 35 to 205 °C at the rate of 3 °C/min and kept isothermally at 205 °C for 10 min. Injector and detector temperature were held, at 250 and 300 °C, respectively. The injected volume was 1 µL of neat oil.

### 2. 2. 6. Gas Chromatography-mass Spectrometry (GC-MS) analysis

Volatile compounds analysis by GC-MS was performed on a gas chromatograph HP 5890 (II) interfaced with a HP 5972 mass spectrometer (Palo Alto, CA, USA) with electron impact ionization (70 eV). A HP-5MS capillary column (30 m × 0.25 mm, 0.25 µm film thickness; Hewlett-Packard, CA, USA) was used. The column temperature was programmed to rise from 50 °C to 240 °C at a rate of 5 °C/min. The carrier gas was helium with a flow rate of 1.2 mL/min; split ratio was 60:1. Scan time and mass range were 1s and 40–300 *m/z*, respectively.

### 2. 2. 8. Volatile Compounds Identification

The identification of the oil constituents was based on a comparison of their retention indices relative to (C<sub>8</sub>-C<sub>22</sub>) *n*-alkanes with those of literature or with those of authentic compounds available in our laboratory. Further identification was made by matching their recorded mass spectra with those stored in the Wiley/NBS mass spectral library of the GC-MS data system and other published mass spectra.<sup>19,20</sup> Quantitative data were obtained from the electronic integration of the FID peak areas.

### 2. 2. 9. Statistical Analysis

All extractions and determinations were conducted in triplicate. Data is expressed as mean ± S.D. Variability in the essential oil yield and composition of the fruits were analyzed by the one-way analysis of variance (ANOVA) followed by Duncan multiple range test using the statistical program package STATISTICA.<sup>21</sup> The differences between individual means were deemed to be significant at *P* > 0.05. Principal component analysis (PCA) was performed in order to determine the relationship between different extraction techniques on the basis of their volatile oil composition.

## 3. Results and Discussion

### 3. 1. Volatile Oil Yield and Composition

The extraction of volatile flavour components from plant matrices is commonly handled by HYD. In addition to this renowned method, other classical methods (SE, S-DHS and SD) were compared with SC-CO<sub>2</sub> in order to select the best one in extraction of the volatile oil from coriander fruits.

### 3. 2. Steam Distillation (SD)

The obtained results demonstrated that the yield of the essential oil extracted from mature fruits by SD is of 0.11% (w/w) which is lower compared to the published data (0.65%).<sup>8</sup> We noticed firstly a prevalence of monoterpene hydrocarbons and esters besides monoterpene alcohols. This class is weekly represented in comparison with the other extraction methods currently used except for S-DHS (Table 1). Three main compounds of the essential oil are identified; linalool (37.31%), limonene (15.68%) and geranyl acetate (13.80%). A different composition was recorded by Ghannadi and Sadeh.<sup>22</sup> In fact, the GC analyses showed that linalool (56.2%), γ-terpinene (12.0%) and δ-3-carene (9.7%) were the most prominent compounds in the essential oil obtained by SD of coriander fruits from Iran. In addition to the relatively low yield recovered by this technique, the use of this method resulted in a notably altered composition of the well-known coriander essential oil. In fact, linalool constitutes more than two-thirds of coriander fruit oil volatiles and is regarded as one of the flavour-impact compounds for fruit essential oil.<sup>23,25</sup> Since, these two facts could be the consequence of a week penetration potential of steam in plant cells. Besides, SD can cause modifications in the composition of the volatile fraction of the extract. Recently, Masango<sup>26</sup> demonstrated that SD is associated with an alteration of essential oil composition due to dissolution of polar compounds in the liquid phase.

### 3. 3. Soxhlet-Dynamic Headspace (S-DHS)

S-DHS extraction, a continuous extraction performed by soxhlet during 6 hours using the hexane as solvent, permitted to assess the oleoresin of coriander fruits at full maturity. Then the volatile compounds were extracted from the oleoresin by dynamic headspace during 3 hours with active charcoal as an adsorbent. According to the French Association of Normalisation,<sup>27</sup> oleoresin constitutes a non aqueous extract with a characteristic odour and/or a flavour that is composed mainly of non volatile constituents obtained from a natural raw material. It contains panoply of soluble material extracted by solvent: odorant products, gustative products, piquant products, fats, waxes, volatile oil. A yield recovered using this method was striking poor (0.002%). Accordingly, the comparison of the yields of the volatile oils extracted from fennel by different methods (soxhlet, sonication, maceration and reflux) showed that the lowest yield was given by soxhlet extraction.<sup>28</sup> Such week yield was probably mainly caused by the mash of the extract with nitrogen, the low capture of the volatile compounds of the extract by the adsorbent and/or their poor desorption or elution. Moreover, the poor yield in volatile oil may be owed to the week extraction of aromatic compounds in versus of the other constituents of the oleoresin such as the waxes, the fats ect. Furthermore, the temperature that induced the boiling

of the extraction solvent could cause a thermal degradation of some volatile compounds. In addition to that we supposed that the use of a low quantity of the plant material can adversely affect the yield.

The list of detected compounds with their retention indices and relative percentages were given in Table 1 in order of their elution on HP-5 column. Main compounds were represented in Table 1 by linalool (28.70%), anethole (9.35%) and *p*-cymen-8-ol (8.63%). The monoterpene alcohols (54.7%) constituted a prevailing terpenic class which is in contrast with the finding of del Valle et al.<sup>29</sup>. In fact, these authors signalled that the soxhlet extraction is often associated with an important percentage of sesquiterpenes particularly their oxygenated form and a low proportion of monoterpenes.

Besides, the observed variations in the volatile oil composition in respect to the classic extraction methods (SD and HYD) are owed to the increased temperature in course of extraction. Consequently, this fact incremented the solubility and accelerated the mass transfer of the aromatic compounds which was conversely associated with a reduction of selectivity.<sup>30</sup> Doubtlessly, it is the cause of the sharp difference concerning the main compounds. Another inconvenient of this extraction method was particularly the interference of some aromatic constituents with the waxes of the oleoresin. This fact could affect the identification and the quantification altogether.<sup>31,32</sup> Furthermore, Vinatoru<sup>28</sup> compared the chemical composition of the volatile oil extracted from fennel using different isolation methods (soxhlet, sonication, maceration and reflux). This same author found that the soxhlet method is rather useful in the extraction of compounds with higher molecular weight in respect to other usually employed methods.<sup>28</sup> In fact, S-DHS extraction is considered to be a “thorough” extraction method for isolation of low volatile compounds because the organic phase cooled from condensation tube continuously passes through the target solid sample for hours. However, poor recovery commonly occurred for extraction of high-volatile or heat-labile compounds.

### 3. 4. Solvent Extraction (SE)

Solvent extraction is a conventional method for isolation of all boiling range volatile compounds, based on their compatibility with organic phase selected. Volatile oil amount obtained by extraction during 30 min is on the range of 0.007%. This extraction method awarded 39 constituents the main amongst them are represented by linalool (56.57%) and geranyl acetate (11.34%). Most abundant terpenic classes were namely the monoterpene alcohols (67.26%) and monoterpene esters (15.3%) (Table 1). This composition was uncommon as compared with literature data. Although all aromatic compounds were isolated in one same step whatever their volatility, the resort to such method is often limited. In fact, the evaporation of

solvent of extraction, in some cases especially in ours (low boiling point solvents), caused the loss in some compounds which explain the week percentage of linalool besides of the degradation and the appearance of other constituents initially not present in the plant material.<sup>33</sup> However, this method seemed to be rather advisable for the isolation of hydrophobic compounds; in fact it ensures the molecular integrity of these constituents known for their thermal stability.<sup>34</sup> The main disadvantage of this technique is solvent-consuming, tedious and, low-recovery for some target compounds.<sup>35</sup> Solvent extraction methods are limited to the compound solubility in the specific solvent used. Because all soluble components are extracted, the extract contains (besides volatile essential oil constituents) semi- or non-volatile di- or triterpenes, which may also be aroma-active. Discrimination of non-volatile, highly volatile, or water-soluble aroma-active components is avoidable according to the solvent used for extraction. On the other hand, resins, fats, and fatty acids, waxes, or pigments are often co-extracted. The composition of the extracts finally does not reflect the proportion of the aroma components in the original material.<sup>36,37</sup>

### 3. 5. Supercritical CO<sub>2</sub> (SC-CO<sub>2</sub>)

Supercritical fluid extraction (SFE) is nowadays in great development and considered consequently as promising alternative to conventional extraction methods. In the volatile oil case, the efficiency of SFE has often been the object of many controversies.<sup>37–40,29</sup> Most SFE used CO<sub>2</sub> as solvent of extraction due to its numerous advantages.<sup>37</sup> In fact, this inert gas is easily eliminated from the extract<sup>38,40</sup> besides of being non toxic, non-flammable and stable chemically, with easy to follow supercritical conditions (critical temperature 31.05 °C, critical pressure 72.9 atm). Table 2 described the experimental conditions of the supercritical CO<sub>2</sub> extraction; this method offered an extract with a maximal yield of 0.45% (w/w) at a pressure of 200 bar, temperature of 40 °C, total CO<sub>2</sub> flow of 235.5 g/min and at a dynamic extraction time of 3 hours. This yield was close to that obtained by Khajeh et al.<sup>41</sup> (5.8%) while, it was sharply higher than that recovered by Anitescu et al.<sup>8</sup>. The employed conditions showed that in the present study the pressure and the total CO<sub>2</sub> flow rate in addition to the fact of using a crushed fruits are the exclusive factors that affected the volatile essence amount.

Varying the pressure value (150 and 200 bar) implied a consistent decrease in volatile oil recovery at 150 bar and a notable increase at 200 bar. This pressure can presumably result in an increase in the SC-CO<sub>2</sub> density which enhances solute solubility and subsequent yield increment. Díaz-Maroto et al.<sup>38</sup> reported that at 200 bar (CO<sub>2</sub> at high density), terpenes and oxygenated compounds were completely miscible in supercritical CO<sub>2</sub>. Fatty acids, waxes and paraffin wax also appeared in the

Table 1: The percentage composition (% w/w) of essential oil of *C. sativum* oils extracted by SD, S-DHS, SE, SC-CO<sub>2</sub> and HD.

| Compounds*                      | RI <sup>a</sup> | RI <sup>b</sup> | SD                              | S-DHS                           | SE                              | SC-CO <sub>2</sub>              | HD                              | df. | F-value  | P         | Identification |
|---------------------------------|-----------------|-----------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|-----|----------|-----------|----------------|
| Heptanal                        | 901             | 1194            | 0.23 ± 0.02 <sup>c</sup>        | 0.04 ± 0.00 <sup>d</sup>        | 0.39 ± 0.04 <sup>a</sup>        | 0.04 ± 0.00 <sup>d</sup>        | tr                              | 4   | 275.500  | 0.0000*** | CG-SM          |
| α-Thujene                       | 931             | 1035            | 0.68 ± 0.07 <sup>a</sup>        | 0.06 ± 0.00 <sup>c</sup>        | 0.09 ± 0.01 <sup>c</sup>        | 0.06 ± 0.00 <sup>c</sup>        | tr                              | 4   | 1197.300 | 0.0000*** | CG-SM          |
| α-Pinene                        | 939             | 1032            | 0.10 ± 0.01 <sup>c</sup>        | 0.03 ± 0.00 <sup>d</sup>        | 0.14 ± 0.01 <sup>bc</sup>       | 0.18 ± 0.01 <sup>b</sup>        | 0.02 ± 0.00 <sup>d</sup>        | 4   | 65.1818  | 0.0000*** | CG-SM, Co-CG   |
| Sabinene                        | 976             | 1132            | 0.21 ± 0.01 <sup>b</sup>        | 0.03 ± 0.00 <sup>c</sup>        | 0.06 ± 0.00 <sup>c</sup>        | 0.21 ± 0.02 <sup>b</sup>        | 0.03 ± 0.00 <sup>c</sup>        | 4   | 165.3750 | 0.0000*** | CG-SM          |
| β-Pinene                        | 980             | 1118            | 0.10 ± 0.01 <sup>b</sup>        | 1.15 ± 0.13 <sup>a</sup>        | 0.11 ± 0.02 <sup>b</sup>        | 0.25 ± 0.03 <sup>b</sup>        | 0.05 ± 0.00 <sup>b</sup>        | 4   | 1110.103 | 0.0000*** | CG-SM, Co-CG   |
| 3-Carene                        | 1011            | 1159            | 0.40 ± 0.03 <sup>d</sup>        | <b>2.05 0.31<sup>a</sup></b>    | 0.20 ± 0.03 <sup>c</sup>        | 1.03 ± 0.12 <sup>c</sup>        | 0.02 ± 0.00 <sup>f</sup>        | 4   | 250.6500 | 0.0000*** | CG-SM          |
| α-Terpinene                     | 1018            | 1188            | 0.33 ± 0.04 <sup>b</sup>        | 0.23 ± 0.03 <sup>c</sup>        | 0.08 ± 0.01 <sup>d</sup>        | 0.44 ± 0.05 <sup>a</sup>        | 0.01 ± 0.00 <sup>e</sup>        | 4   | 139.4583 | 0.0000*** | CG-SM, Co-CG   |
| p-Cymene                        | 1026            | 1280            | 0.68 ± 0.07 <sup>b</sup>        | 0.31 ± 0.01 <sup>c</sup>        | 0.15 ± 0.02 <sup>e</sup>        | 0.24 ± 0.04 <sup>d</sup>        | tr                              | 4   | 210.0978 | 0.0000*** | CG-SM, Co-CG   |
| Limonene                        | 1030            | 1203            | <b>15.68 ± 1.66<sup>a</sup></b> | 0.10 ± 0.01 <sup>d</sup>        | 0.14 ± 0.02 <sup>cd</sup>       | 0.16 ± 0.02 <sup>c</sup>        | 0.02 ± 0.00 <sup>e</sup>        | 4   | 64405.7  | 0.0000*** | CG-SM, Co-CG   |
| 1,8-Cineole                     | 1033            | 1213            | 0.03 ± 0.00 <sup>e</sup>        | 0.45 ± 0.06 <sup>c</sup>        | 2.17 ± 0.30 <sup>b</sup>        | 0.41 ± 0.05 <sup>c</sup>        | 0.20 ± 0.03 <sup>d</sup>        | 4   | 269.9712 | 0.0000*** | CG-SM, Co-CG   |
| (Z)-β-Ocimene                   | 1040            | 1246            | 0.41 ± 0.04 <sup>c</sup>        | 0.16 ± 0.02 <sup>c</sup>        | 0.28 ± 0.02 <sup>d</sup>        | 1.78 ± 0.22 <sup>a</sup>        | tr                              | 4   | 5934.000 | 0.0000*** | CG-SM, Co-CG   |
| γ-Terpinene                     | 1062            | 1266            | <b>3.22 ± 0.44<sup>a</sup></b>  | 0.10 ± 0.01 <sup>c</sup>        | 0.69 ± 0.08 <sup>c</sup>        | 2.00 ± 0.22 <sup>b</sup>        | tr                              | 4   | 28.5971  | 0.0000*** | CG-SM, Co-CG   |
| Cis-Linalool oxide (Furanoid)   | 1074            | 1478            | 2.48 ± 0.25 <sup>b</sup>        | 1.44 ± 0.16 <sup>c</sup>        | 0.13 ± 0.01 <sup>f</sup>        | <b>2.79 ± 0.31<sup>a</sup></b>  | 0.27 ± 0.03 <sup>e</sup>        | 4   | 6603.838 | 0.0000*** | CG-SM          |
| Terpinolene                     | 1088            | 1290            | 2.89 ± 0.32 <sup>a</sup>        | 0.21 ± 0.03 <sup>c</sup>        | 0.68 ± 0.07 <sup>c</sup>        | <b>2.26 ± 0.28<sup>b</sup></b>  | 0.15 ± 0.01 <sup>f</sup>        | 4   | 6777.300 | 0.0000*** | CG-SM, Co-CG   |
| trans-linalool oxide (Furanoid) | 1088            | 1450            | 0.21 ± 0.02 <sup>c</sup>        | 0.19 ± 0.02 <sup>cd</sup>       | 0.17 <sup>d</sup>               | 0.93 <sup>a</sup>               | tr                              | 4   | 1637.500 | 0.0000*** | CG-SM          |
| <b>Linalool</b>                 | 1088            | 1553            | <b>37.31 ± 4.22<sup>d</sup></b> | <b>28.70 ± 3.12<sup>f</sup></b> | <b>56.57 ± 6.21<sup>c</sup></b> | <b>78.27 ± 8.05<sup>b</sup></b> | <b>87.54 ± 9.45<sup>a</sup></b> | 4   | 1016.155 | 0.0000*** | CG-SM, Co-CG   |
| Camphor                         | 1143            | 1532            | 0.09 ± 0.00 <sup>f</sup>        | 0.95 ± 0.02 <sup>b</sup>        | 0.17 ± 0.03 <sup>d</sup>        | 0.36 ± 0.04 <sup>c</sup>        | 0.17 ± 0.02 <sup>d</sup>        | 4   | 627.6571 | 0.0000*** | CG-SM          |
| Borneol                         | 1165            | 1719            | 0.40 ± 0.05 <sup>d</sup>        | 0.97 ± 0.08 <sup>b</sup>        | 1.72 ± 0.18 <sup>a</sup>        | 0.56 ± 0.06 <sup>c</sup>        | 0.34 ± 0.04 <sup>de</sup>       | 4   | 105.200  | 0.0000*** | CG-SM          |
| Menthol                         | 1173            | 1628            | 0.20 ± 0.03 <sup>b</sup>        | 0.89 ± 0.09 <sup>a</sup>        | 0.03 ± 0.00 <sup>c</sup>        | 0.24 ± 0.03 <sup>b</sup>        | 0.05 ± 0.00 <sup>c</sup>        | 4   | 35.0336  | 0.0000*** | CG-SM          |
| Terpinene-4-ol                  | 1178            | 1611            | 0.27 ± 0.03 <sup>c</sup>        | 1.23 ± 0.11 <sup>a</sup>        | nd                              | 0.11 ± 0.01 <sup>d</sup>        | tr                              | 4   | 2891.464 | 0.0000*** | CG-SM, Co-CG   |
| p-Cymen-8-ol                    | 1183            | 1864            | 1.89 ± 0.19 <sup>b</sup>        | <b>8.63 ± 0.95<sup>a</sup></b>  | 0.08 ± 0.00 <sup>e</sup>        | 0.13 ± 0.01 <sup>d</sup>        | tr                              | 4   | 103210.7 | 0.0000*** | CG-SM, Co-CG   |
| cis-Hex-3-enyl butyrate         | 1188            | 1485            | 0.37 ± 0.04 <sup>a</sup>        | 0.02 ± 0.00 <sup>c</sup>        | 0.36 ± 0.04 <sup>a</sup>        | 0.14 ± 0.01 <sup>b</sup>        | 0.01 ± 0.00 <sup>c</sup>        | 4   | 203.1522 | 0.0000*** | CG-SM          |
| α-Terpineol                     | 1189            | 1706            | 0.20 ± 0.03 <sup>b</sup>        | 0.20 ± 0.02 <sup>b</sup>        | 0.27 ± 0.03 <sup>b</sup>        | 0.09 ± 0.01 <sup>c</sup>        | 0.05 ± 0.00 <sup>c</sup>        | 4   | 5.7918   | 0.0111*   | CG-SM, Co-CG   |
| Cis-Dihydrocarvone              | 1193            | 1645            | nd                              | 1.26 ± 0.13 <sup>b</sup>        | 0.18 ± 0.01 <sup>d</sup>        | 0.12 ± 0.01 <sup>de</sup>       | <b>2.36 ± 0.25<sup>a</sup></b>  | 4   | 15460.20 | 0.0000*** | CG-SM          |
| Nerol                           | 1228            | 1797            | 1.02 ± 0.12 <sup>c</sup>        | <b>2.56 ± 0.28<sup>b</sup></b>  | 0.05 ± 0.00 <sup>d</sup>        | 0.09 ± 0.00 <sup>d</sup>        | tr                              | 4   | 18138.45 | 0.0000*** | CG-SM          |
| β-Citronellol                   | 1228            | 1772            | 1.14 ± 0.12 <sup>b</sup>        | 0.58 ± 0.06 <sup>c</sup>        | 1.18 ± 0.15 <sup>a</sup>        | 0.09 ± 0.00 <sup>e</sup>        | 0.52 ± 0.08 <sup>d</sup>        | 4   | 1859.294 | 0.0000*** | CG-SM          |
| Neral                           | 1240            | 1694            | nd                              | 1.18 ± 0.13 <sup>b</sup>        | 0.44 ± 0.07 <sup>c</sup>        | 0.27 ± 0.03 <sup>d</sup>        | 0.13 ± 0.01 <sup>e</sup>        | 4   | 976.9545 | 0.0000*** | CG-SM          |
| Carvone                         | 1242            | 1751            | 0.73 ± 0.08 <sup>c</sup>        | 0.69 ± 0.07 <sup>c</sup>        | 0.82 ± 0.08 <sup>a</sup>        | 0.14 ± 0.01 <sup>d</sup>        | 0.08 ± 0.00 <sup>e</sup>        | 4   | 981.0789 | 0.0000*** | CG-SM, Co-CG   |
| Geraniol                        | 1255            | 1857            | <b>3.56 ± 0.36<sup>a</sup></b>  | 0.64 ± 0.08 <sup>c</sup>        | 1.81 ± 0.21 <sup>b</sup>        | 0.45 ± 0.05 <sup>d</sup>        | tr                              | 4   | 7164.663 | 0.0000*** | CG-SM, Co-CG   |
| Geranial                        | 1270            | 1742            | nd                              | 0.14 ± 0.01 <sup>c</sup>        | 2.14 ± 0.22 <sup>a</sup>        | 0.19 ± 0.02 <sup>c</sup>        | 0.03 ± 0.00 <sup>d</sup>        | 4   | 5771.932 | 0.0000*** | CG-SM          |
| Anethole                        | 1283            | 1828            | nd                              | <b>9.35 ± 1.02<sup>a</sup></b>  | <b>4.37 ± 0.56<sup>b</sup></b>  | 0.28 ± 0.04 <sup>c</sup>        | 0.01 ± 0.00 <sup>d</sup>        | 4   | 76501.68 | 0.0000*** | CG-SM          |
| Thymol                          | 1290            | 2198            | 2.34 ± 0.25 <sup>b</sup>        | <b>3.41 ± 0.36<sup>a</sup></b>  | 2.02 ± 0.33 <sup>c</sup>        | 0.09 ± 0.00 <sup>f</sup>        | <b>1.85 ± 0.20<sup>d</sup></b>  | 4   | 4594.053 | 0.0000*** | CG-SM, Co-CG   |
| Carvacrol                       | 1292            | 2239            | nd                              | 0.57 ± 0.06 <sup>b</sup>        | 0.68 ± 0.08 <sup>a</sup>        | 0.22 ± 0.02 <sup>d</sup>        | 0.46 ± 0.04 <sup>e</sup>        | 4   | 872.076  | 0.0000*** | CG-SM          |
| δ-Elementene                    | 1339            | 1479            | nd                              | 0.62 ± 0.07 <sup>b</sup>        | 0.31 ± 0.04 <sup>c</sup>        | 0.26 ± 0.02 <sup>d</sup>        | 0.01 ± 0.00 <sup>e</sup>        | 4   | 1623.544 | 0.0000*** | CG-SM          |
| Eugenol                         | 1356            | 2192            | 2.13 ± 0.22 <sup>a</sup>        | 0.95 ± 0.09 <sup>c</sup>        | 1.18 ± 0.12 <sup>b</sup>        | 0.33 ± 0.04 <sup>d</sup>        | 0.01 ± 0.00 <sup>e</sup>        | 4   | 4414.602 | 0.0000*** | CG-SM, Co-CG   |
| Neryl acetate                   | 1356            | 1733            | nd                              | 0.83 ± 0.09 <sup>c</sup>        | 3.96 ± 0.46 <sup>a</sup>        | 1.08 ± 0.12 <sup>b</sup>        | tr                              | 4   | 28514.79 | 0.0000*** | CG-SM          |
| Geranyl acetate                 | 1383            | 1765            | <b>13.80 ± 1.45<sup>a</sup></b> | 0.25 ± 0.03 <sup>f</sup>        | <b>11.34 ± 1.53<sup>c</sup></b> | <b>0.56 ± 0.06<sup>e</sup></b>  | <b>0.83 ± 0.09<sup>d</sup></b>  | 4   | 43874.24 | 0.0000*** | CG-SM, Co-CG   |
| β-Caryophyllene                 | 1418            | 1612            | 0.68 ± 0.08 <sup>a</sup>        | 0.05 ± 0.00 <sup>d</sup>        | 0.34 ± 0.03 <sup>b</sup>        | 0.12 ± 0.01 <sup>c</sup>        | 0.03 ± 0.00 <sup>de</sup>       | 4   | 429.9808 | 0.0000*** | CG-SM          |
| α-Humulene                      | 1454            | 1687            | 1.17 ± 0.12 <sup>c</sup>        | <b>3.67 ± 0.42<sup>b</sup></b>  | nd                              | 0.67 ± 0.07 <sup>d</sup>        | 0.02 ± 0.00 <sup>e</sup>        | 4   | 26454.58 | 0.0000*** | CG-SM          |
| Germacrene-D                    | 1480            | 1726            | 0.88 ± 0.09 <sup>a</sup>        | 0.08 ± 0.00 <sup>b</sup>        | nd                              | 0.07 ± 0.00 <sup>bc</sup>       | 0.05 ± 0.00 <sup>c</sup>        | 4   | 1600.731 | 0.0000*** | CG-SM          |
| Eugenyl acetate                 | 1524            | nd              | 2.56 ± 0.32 <sup>b</sup>        | <b>2.77 ± 0.31<sup>a</sup></b>  | nd                              | 0.10 ± 0.01 <sup>d</sup>        | 0.07 ± 0.00 <sup>d</sup>        | 4   | 30717.75 | 0.0000*** | CG-SM          |

|                                    |                                  |                                  |                                   |                                  |                                   |   |          |            |  |  |
|------------------------------------|----------------------------------|----------------------------------|-----------------------------------|----------------------------------|-----------------------------------|---|----------|------------|--|--|
| <b>Grouped compounds</b>           |                                  |                                  |                                   |                                  |                                   |   |          |            |  |  |
| Monoterpene hydrocarbons           | 23.34 ± 3.12 <sup>a</sup>        | 4.06 ± 0.52 <sup>d</sup>         | 2.38 ± 0.25 <sup>e</sup>          | 8.31 ± 0.97 <sup>c</sup>         | 0.30 ± 0.04 <sup>f</sup>          | 4 | 56180.16 | 0.0000**** |  |  |
| Aromatic hydrocarbons              | 0.68 ± 0.07 <sup>b</sup>         | 0.31 ± 0.03 <sup>c</sup>         | 0.15 ± 0.01 <sup>e</sup>          | 0.24 ± 0.02 <sup>d</sup>         | tr                                | 4 | 210.097  | 0.0000**** |  |  |
| Monoterpene Alcohols               | 48.12 ± 5.41 <sup>e</sup>        | 54.70 ± 6.42 <sup>d</sup>        | 67.26 ± 7.84 <sup>c</sup>         | 80.64 ± 9.83 <sup>b</sup>        | 88.52 ± 9.56 <sup>a</sup>         | 4 | 45432.37 | 0.0000**** |  |  |
| Phenols                            | 2.34 ± 0.32 <sup>c</sup>         | 3.98 ± 0.42 <sup>a</sup>         | 2.70 ± 0.33 <sup>b</sup>          | 0.31 ± 0.03 <sup>e</sup>         | 2.31 ± 0.24 <sup>c</sup>          | 4 | 616.7310 | 0.0000**** |  |  |
| Monoterpene esters                 | 16.36 ± 1.83 <sup>a</sup>        | 3.85 ± 0.42 <sup>d</sup>         | <b>15.30</b> ± 1.66 <sup>b</sup>  | 1.74 ± 0.18 <sup>e</sup>         | 0.90 ± 0.08 <sup>f</sup>          | 4 | 7643.265 | 0.0000**** |  |  |
| Monoterpene ketones                | 0.82 ± 0.07 <sup>e</sup>         | 2.90 ± 0.35 <sup>b</sup>         | 1.17 ± 0.14 <sup>d</sup>          | 0.62 ± 0.08 <sup>f</sup>         | <b>2.61</b> ± 0.31 <sup>c</sup>   | 4 | 1480.394 | 0.0000**** |  |  |
| Monoterpene aldehydes              | 0.68 ± 0.07 <sup>d</sup>         | 1.32 ± 0.15 <sup>c</sup>         | 2.58 ± 0.29 <sup>b</sup>          | 0.46 ± 0.05 <sup>e</sup>         | 0.16 ± 0.01 <sup>f</sup>          | 4 | 2661.346 | 0.0000**** |  |  |
| Monoterpene ethers                 | 2.72 ± 0.28 <sup>c</sup>         | 2.08 ± 0.21 <sup>e</sup>         | 2.47 ± 0.29 <sup>d</sup>          | 4.13 ± 0.55 <sup>b</sup>         | 0.47 ± 0.05 <sup>f</sup>          | 4 | 1366.603 | 0.0000**** |  |  |
| Sesquiterpenes                     | 2.73 ± 0.30 <sup>c</sup>         | <b>4.42</b> ± 0.52 <sup>b</sup>  | 0.65 ± 0.08 <sup>e</sup>          | 1.12 ± 0.14 <sup>d</sup>         | 0.11 ± 0.01 <sup>e</sup>          | 4 | 10787.90 | 0.0000**** |  |  |
| Non terpenics                      | 0.23 ± 0.03 <sup>c</sup>         | 0.04 ± 0.00 <sup>d</sup>         | 0.39 ± 0.04 <sup>a</sup>          | 0.04 ± 0.00 <sup>d</sup>         | tr                                | 4 | 275.500  | 0.0000**** |  |  |
| Others                             | 0.37 ± 0.04 <sup>a</sup>         | 0.02 ± 0.00 <sup>c</sup>         | 0.36 ± 0.04 <sup>a</sup>          | 0.14 ± 0.01 <sup>b</sup>         | 0.01 ± 0.00                       | 4 | 466.730  | 0.0000**** |  |  |
| <b>Total identified (%)</b>        | <b>98.39</b> ± 9.45 <sup>a</sup> | <b>77.74</b> ± 8.96 <sup>c</sup> | <b>95.50</b> ± 10.25 <sup>c</sup> | <b>97.81</b> ± 9.48 <sup>b</sup> | <b>95.39</b> ± 10.75 <sup>d</sup> | 4 | 556.730  | 0.0000**** |  |  |
| <b>Essential oil yield (% w/w)</b> | 0.11 ± 0.01 <sup>c</sup>         | 0.002 ± 0.00 <sup>e</sup>        | <b>0.007</b> ± 0.00 <sup>d</sup>  | <b>0.45</b> ± 0.06 <sup>a</sup>  | <b>0.34</b> ± 0.05 <sup>b</sup>   | 4 | 57.39286 | 0.0000**** |  |  |

tr: trace (>0.01%), nd: not detected. Volatile compounds percentages in the same line with different letters (a–e) are significantly different at  $P > 0.05$ . Bold values have been used for showing the main representative compounds.

<sup>a</sup> Order of elution in apolar column (HP-5).

<sup>b</sup> Order of elution in polar column (HP-Innowax).

SD: Steam distillation, S-DHS: Soxhlet-dynamic headspace, SE: Solvent extraction, CO<sub>2</sub>: Supercritical CO<sub>2</sub>, HD: Hydrodistillation.

\*  $P > 0.05$ . \*\*\*\*  $P > 0.001$ .

extract explaining the high extract yield (4.5%) recorded in the current study. Moreover, changes in the total CO<sub>2</sub> flow resulted in the yield fluctuations. Since, increasing of the CO<sub>2</sub> flow rate more than 235.5 g/min induced a systematic drop in volatile oil amount. Another detrimental factor should be highlighted is the use of crushing coriander fruits; this study showed that entire non crushed extract of fruits exhibited a significant low yield (0.12%) in respect to the yield reached following the grinding of the fruits (4.5%). In agreement with our findings, Ferraro et al.<sup>42</sup> showed that the efficiency of SC–CO<sub>2</sub> increased with the decrease of particle size of the plant material. As whole, extraction of crushed fruits at a total CO<sub>2</sub> flow rate of 235.5 g/min and a pressure of 200 bar constituted optimal extraction conditions that guarantee a maximal yield. Apparently, SC–CO<sub>2</sub> is the best technique since it offered a maximal yield but the resort to such high pressure (200 bar) caused an additional extraction of non-volatile constituents along with the volatile ones resulting in the elevated observed yield.<sup>38</sup> The volatile composition is mostly prevailed by monoterpene alcohols (80.64%), and monoterpene hydrocarbons (8.31%). The main constituents were represented by linalool (78.27%), *cis*-linalool oxide (2.79%) and terpinolene (2.26%). This composition differed from that described by Illès et al.<sup>11</sup> Coriander samples studied by this author were particularly rich in linalool (70%), geranyl acetate (7%) and linalyl acetate (0.3%). Linalool (61.9%), *p*-cymene (4%),  $\delta$ -terpinene (3.5%),  $\alpha$ -pinene (2.8%) and limonene (2.7%) were the main constituents of seeds volatile oil isolated by the same method according to Anitescu et al.<sup>8</sup>

However, standard methods of extraction are lacking in despite of the substantial data on SFE. This is due to different preparation techniques of the extract as well as the choice of analytical parameters. This subsequently induces sharply qualitative and quantitative variations.<sup>41</sup> In addition to differences dependant of the origin, the scale, the pedoclimatic factors, the choice of the extraction solvent,<sup>11</sup> the analytical parameters notably the temperature and the pressure are detrimental factors affecting the quality of the extract obtained by SFE. At 200 bar, the CO<sub>2</sub> is at high density and subsequently may cause changes in the sample oil quality explaining the lower linalool percentage in respect to HYD. The process at high pressure seemed to be less convenient to obtain the high-volatile compounds but favoured the extraction of waxes. Accordingly, Zorca et al.<sup>43</sup> found that the compounds isolated by HYD were practically the same as those extracted by the SFE process while the higher percentages were found in supercritical oil (SFE) rather than in hydrodistilled oil (HYD) mainly linalool which consisted of 72.10% in supercritical oil versus 45.31% in hydrodistilled oil. The higher percentages of the compounds in SFE were owed to the fractional precipitation technique which was very selective since no paraffin precipitated together with the oil extracted by SFE.<sup>43</sup>

**Table 2:** SFE experimental conditions and extraction yields of *C. sativum*.

| Run no. | Pressure (bar) | Temperature °C | Dynamic Time (H) | Crushing | Total CO <sub>2</sub> debit (g) | Extraction yield (% w/w) |
|---------|----------------|----------------|------------------|----------|---------------------------------|--------------------------|
| 1       | 200            | 40             | 3                | –        | 442                             | 0.39 ± 0.03 <sup>b</sup> |
| 2       | 200            | 40             | 3                | +        | 300                             | 0.37 ± 0.02 <sup>c</sup> |
| 3       | 150            | 40             | 3                | +        | 317                             | 0.12 ± 0.01 <sup>e</sup> |
| 4       | 200            | 40             | 3                | +        | 235.5                           | 0.45 ± 0.03 <sup>a</sup> |
| 5       | 200            | 40             | 3                | +        | 845                             | 0.27 ± 0.02 <sup>d</sup> |

Extraction yield percentages in the same column with different letters (a–e) are significantly different at  $P > 0.05$ .

However, Luque de Castro et al.<sup>37</sup> showed that temperature of 40 °C and pressures ranging from 83 to 124 bar favoured the terpene extraction. So, the SC–CO<sub>2</sub> still offers a neat advantage over the other methods for volatiles extraction if these two parameters were taken in account in order to minimize the occurrence of undesirable non volatile compounds. Moreover, SC–CO<sub>2</sub> extraction has different advantages over conventional methods such as low operating temperature, thus no thermal degradation of most of the labile compounds and the omission of the evaporation step lead to avoid any lose of the high-volatile components and make of this technique a best choice. SC–CO<sub>2</sub> extraction also, seems to be a cost-effective process at laboratory scale. Therefore, it can be recommended as a suitable extraction method to isolate volatile compounds from coriander fruits.

### 3. 6. Hydrodistillation (HYD)

In course of HYD, the extraction of the compounds from the structures of biosynthesis and/or of storage of the essential oil depends on two principal factors, the hydro-diffusion and the boiling point of the volatile compounds.<sup>44</sup> As regards the hydro-diffusion, the compounds are dissolved in water before their diffusion to the surface of fruit where they are volatilised.<sup>44</sup>

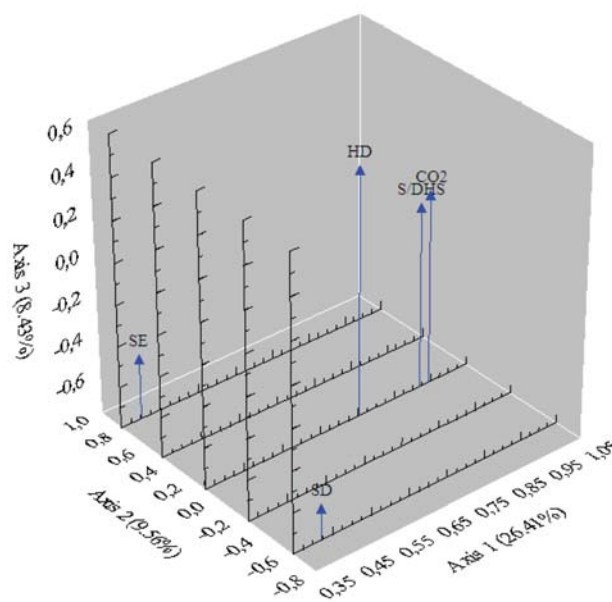
The essential oil presented a fairly good amount (0.34%) in respect with that given by other applied methods. This yield was in accordance with literature data. Hence, the HYD of coriander seeds in provenance of eight regions from India furnished a yield ranging from 0.18 to 0.39%.<sup>45</sup> Table 1 showed the essential oil composition obtained by HYD with identification of 95.34% of the total compounds. The monoterpene alcohols were the prominent terpenic class accounting for 88.52% (Table 1). The linalool (87.54%), the *cis*-dihydrocarvone (2.36%), the thymol (1.85%) and the geranyl acetate (0.83%) prevailed as compared with the remaining compounds which for the most occurred in very low proportions or in traces. Generally, the essential oil profile obtained by this method is in accordance with literature data. Hence, the essential oil extracted by the HYD of coriander seeds from India revealed the occurrence of 30 compounds predominated by linalool (56.71–75.14%).<sup>45</sup> Other studies conducted on coriander seeds from India exhibited a

prevalence of linalool (75.30%), geranyl acetate (8.12%) and  $\alpha$ -pinene (4.09%).<sup>46</sup> Likewise, linalool (69.8%),  $\alpha$ -pinene (5.4%),  $\gamma$ -terpinene (5.3%), camphor (5.2%) and  $\beta$ -myrcene (1.5%) are the major compounds of the essential oil of coriander produced and commercialized by Northern Essentials (Prince Albert, SK, Canada).<sup>47</sup>

The main advantage of this method is its selectivity to extract volatile compounds. Since, during HYD only the steam-volatile ingredients of aromatic plants can be extracted. Non-volatile aroma compounds are, of course, not extracted with HYD.

### 3. 7. Comparison Between the Employed Techniques

In order to determine the relationship between the different extractions on the basis of their volatile oils composition, principal component analysis (PCA) was carried out. A better discrimination was revealed on the three-dimensional visualization of the plotted scores, where the



**Figure 2:** Principal component analysis of coriander essential oils extracted by different techniques (Table 2). SD: Steam distillation, S-DHS: Soxhlet-dynamic headspace, SE: Solvent extraction, CO<sub>2</sub>: Supercritical CO<sub>2</sub>; HD: Hydrodistillation.



three PC accounted for 44.4% of total variance. As shown in Figure 2, SC-CO<sub>2</sub>, S-DHS and HYD were grouped together; SE and SD were distinguished from the first group. On the other hand, it is worthy to note that the oil constituents were highly affected ( $P > 0.001$ ) by the extraction technique (Table 1) except for the  $\alpha$ -terpineol, the fluctuations of its percentage were weekly afforded to the extraction method. This later compound showed the relative stability which could be explained by its genetic determinism.

Among the different extraction methods, differences concerning the composition of the components are well recognizable (Table 1). Firstly, we noticed that all the extraction procedures are to be classified as clearly more sparing to the genuine components by preventing the transformation of the main compound except for S-DHS and SD. For coriander fruits currently investigated, non-volatile substances resulting in the observed alteration in the composition of the coriander oil could not occur in the hydrodistillates, in contrast to the SE and SC-CO<sub>2</sub> extracts. These transformations are poorly studied, so the modifications we found in the oil composition can find only a partial explanation based on the studies of the reactivity of individual terpenes and model systems.

The obtained oils by SC-CO<sub>2</sub> and HYD were dominated by monoterpene alcohols, linalool being the principal constituent.<sup>42</sup> These results were similar to those obtained by others authors.<sup>48,8,44</sup> However, SD and S-DHS offered volatile oils marked by striking decreased monoterpene alcohols and an incremented monoterpene hydrocarbons and esters in one hand and sesquiterpenes in another hand. SE contains more highly volatile components compared to SD and S-DHS extractions, probably due to the characteristics of long lasting boiling which occurred in course of S-DHS extraction and the incompatibility of these compounds with water steam in SD. The clear limitation of SE and of SD is due to their open extraction system and following step-liquid-liquid extraction. During this procedure, not only high-volatile components such as linalool oxide, linalyle acetate and linalool and so forth had a chance to escape from the distillation system, but the analytes hardly transferred to organic phase.

S-DHS extraction can almost “exhaustively” extract all the low-volatile compounds compared with HYD and SC-CO<sub>2</sub>. These findings indicate that S-DHS was suitable for high-boiling point compounds. As for the high-volatile component, HYD and SC-CO<sub>2</sub> were appreciated as reported by Gu et al.<sup>49</sup>

Volatile compounds of plants have usually been extracted by conventional extraction methods such as solvent extraction and steam distillation. Some of the main disadvantages of these methods include: long extraction time, losses of volatile compounds and degradation of unsaturated compounds, resulting unfavourable off-flavour compounds due to heat.

However, the use of HYD for the subsequent determination of the aroma compounds composition has often

been discussed very critically because of transformation processes of genuine aroma-active compounds due to the influence of heat, steam, and pH.<sup>50–52</sup>

In supercritical fluid extraction (SFE) supercritical carbon dioxide acts as an organic solvent. With SFE the extraction conditions can also be adapted by variation of temperature and pressure. Compared to solvent-extracted oleoresins, supercritical fluid extracts are free of any solvent, what is the main advantage for food industrial use.<sup>53,54</sup>

## 4. Conclusions

Overall, the results reported on the chemical composition of the essential oil of the coriander fruit revealed great differences occurring during extraction process. The SC-CO<sub>2</sub> still offers a neat advantage over the other methods for volatiles extraction at optimal pressure in order to ensure maximal yield and a minimum of undesirable non volatile compounds. Our data suggest that the growing use of essential oil of coriander fruit in various fields of human activity requires consideration of the effects of extraction process on the genuine composition and quality of this product.

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## Povzetek

Eterična olja iz semen koriandra (*Coriandrum sativum* L.) so bila izolirana z uporabo različnih tehnik ekstrakcije in destilacije, kot so konvencionalna ekstrakcija, »Soxhlet-dynamic headspace« (S-DHS), superkritična ekstrakcija s CO<sub>2</sub>, destilacija z vodno paro in vodna destilacija. GC-FID in GC-MS analize dobljenih eteričnih olj so pokazale, da med detektiranimi in identificiranimi spojinami v vseh teh oljih prevladuje linalol, kar je karakteristično za tunizijska koriandrova eterična olja. S statistično analizo je bilo potrjeno, da je vsebnost vseh ostalih komponent razen  $\alpha$ -terpineola odvisna od načina in pogojev izolacije eteričnih olj. Dokazano je bilo tudi, da je sestava eteričnih olj dobljenih z vodno destilacijo, s S-DHS in s superkritično ekstrakcijo s CO<sub>2</sub> podobna. Med uporabljenimi tehnikami ekstrakcije in destilacije je bila superkritična ekstrakcija s CO<sub>2</sub> najbolj učinkovita.