Cinnamon bark volatile oils separation and determination using solid-phase extraction and gas chromatography

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Abstract

One of the SPE method is reversed phase separation which involve a polar usually aqueous or moderately polar sample matrix (mobile phase) and a nonpolar stationary phase. The analyte of interest is typically mid- to non polar. Several SPE materials are in the reversed phase category including C18. The hydrophilic silanol groups at the surface of the raw silica packing have been chemically modified with hydrophobic alkyl functional groups by reaction with the corresponding silanes. Retention of organic analytes from polar solutions on to the SPE materials is due primarily to attractive forces between the carbon-hydrogen bonds in the analyte and the functional group in the silica surface. These nonpolar-nonpolar attractive forces are van der waals forces. In this work, at first the aqueous solutions of Cinnamomum zeylanicum Blume bark were obtained by hydrodistillation and superheated water extraction (SWE) methods, then main the volatile compounds were extracted from aqueous solutions by solid phase extraction (SPE) method. This method involves adsorption of the desired components on C18 SEP PAK (Monofunctional -Si (CH3)2C18H37), followed by desorption in the desorption chamber, using minimum volume solvent as the mobile phase. Solid phase extraction conditions optimized on C18 SEP PAK classic cartridge. Different solvent including acetone, hexane, ethyl acetate, ethanol, and mix methanol: water were examined. A good separation of E-cinnamaldehyde was obtained on the adsorbent column. The amount of extracted essential oil composition of C. zeylanicum by SPE, evaluated in different conditions. Gas chromatography/mass spectrometry and gas chromatography were used to identify and quantity the volatile compound composition. GC analysis showed that the maximum yield of E-cinnamaldehyde obtained by methanol: water in (70:30 v/v) ratio by SPE extraction. At the optimum condition, the GC results indicated that E-cinnamaldehyde was the highest area percentage of 79.60% in the volatile oils extracted by hydrodistillation and 88.50% by superheated water extraction.

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1. Introduction

The principle of SPE is similar to liquid-liquid extraction (LLE), involving a partitioning of solutes between two phases. However, instead of two immiscible liquid phases, as in LLE, SPE involves partitioning between a liquid (sample matrix or solvent with analytes) and a solid (sorbent) phase. This sample treatment technique enables the concentration and purification of analytes from solution by sorption on a solid sorbent and purification of extract after extraction [1]. An SPE device consists of a resin bed packed into a small extraction tube, usually made of plastic. The resin is packed between two frits to hold the resin bed securely in place. A liquid sample is passed through the resin bed by applying either positive pressure or vacuum to the column [2].

A typical procedure of solid phase extraction involves four steps. First, the column is conditioned with an appropriate solvent to solvate functional groups of the sorbent. After the sorbent is further conditioned with the sample matrix solvent, the sample solution is forced through the sorbent by aspiration or positive pressure. The column containing retained analyte is subsequently washed with an appropriate solvent that selectively elutes impurities but leaves the analyte on the column. The purified analyte is finally eluted with a solvent strong enough to displace the analyte from the sorbent.

The mechanisms involved in solid phase extraction are normal phase, reversed phase and Ion exchange chromatography that are explained respectively.

Normal phase chromatography whose procedures typically involve a polar analyte, a mid-to nonpolar matrix (e.g. acetone, chlorinated solvents, and hexane), and a polar stationary phase. Polar-functionalized bonded silicas (e.g. LC-CN, LC-NH2, and LC-Diol), and polar adsorption media (LC-Si, LC-Florisil, ENV1-Florisil, and LC-Alumina) are typically used under normal phase conditions. Retention of an analyte under normal phase conditions is primarily due to interactions between polar functional groups of the analyte and polar groups on the sorbent surface. These include hydrogen bonding, pi-pi interactions, dipole-dipole interactions, and dipole-induced dipole interactions, among others. A compound adsorbed by these mechanisms is eluted by passing a solvent that disrupts the binding mechanism — usually a solvent that is more polar than the sample’s original matrix.

Reversed phase chromatography whose procedures involve a polar (usually aqueous) or moderately polar sample matrix (mobile phase) and a nonpolar stationary phase. The analyte of interest is typically mid-to nonpolar. Several SPE materials, such as alkyl- or aryl-bonded silicas (LC-18, ENV1-18, LC-8, ENV1-8, LC-4, and LC-Ph) are in the reversed phase category. Ion exchange chromatography that can be used for compounds which are charged when in a solution (usually aqueous, but sometimes organic) [3].

As far as essential oils are concerned, solid phase extraction (SPE) is used for their pre-separation and fractionation prior to gas chromatographic analysis as well as after superheated water extraction (SWE). According to Antonelli and Fabbri [4], essential oils can be divided in two categories – the former one includes essential oils which are very complex mixtures whose components belong to different classes of compounds and the latter one consists of essential oils with one major component comprising up to 90% with a few other minor compounds which can be important for the quality and difficult to identify. That is why silica SPE is needed for pre-separation of essential oils which consequently leads to formation of three fractions: the first one containing all hydrocarbons, both saturated and unsaturated, the second one which contains carbonyl compounds, ethers, esters and tertiary alcohols and the third one containing primary alcohols, acids and diols. Such a fractionation helps to avoid problems with peak overlapping or co eluting substances as well as to facilitate the concentration of remaining fractions after removal of the
major compound in the latter group of essential oils. As a frequent aim of SWE is to avoid the use of organic solvents, it is suggested to apply extraction methods that are solvent free or use minimal amounts of solvents. SPE is exactly such a technique which enables extraction of retained analytes with a small volume of elution solvent [5].

An endcapped C18 SPE cartridge was used after superheated water extraction of fragrance compounds from Rosa canina. In this case, a solvent used for elution was hexane and identified compounds were mainly benzyl alcohol, benzaldehyde, phenylethyl alcohol, 2,6,11-trimethyl dodecane, eicosane, tetrahydroional and limonene [6].

The most frequently used sorbent in the analysis of volatile components is octadecyl (C18) that enables reversed phase extraction of mid-to nonpolar analytes.

A column with such a stationary phase was utilized in the analysis of volatile compounds of Rosa damascena after extraction with superheated water, which is obligatory when extracting essential oils on a laboratory scale. For elution, a mixture of hexane and ethyl acetate was used and there were 37 eluted and identified components with percentage higher than 0.05%. The major ones were linalool, phenylethyl alcohol, citronellol, nerol and geraniol [7].

An identical procedure with the same sorbent and eluent was applied for re-extracting analytes from the aqueous extract of Origanum onites, which are mainly carvacrol, borneol, terpinen-4-ol, α-terpineol, thymol and linalool [8], as well as in the work concerning essential oils of Achillea monocephala leaves and flowers. The major compounds were camphor and borneol for the leaf oil and camphor, borneol, 1,8-cineole and α-campholenal for the flower oil [9]. Dichloromethane was used for elution of compounds retained on C18 cartridge while isolating the volatile and semi-volatile compounds of Salvia officinalis leaves infusion. These compounds were α-thujone, camphor, 1,8-cineole, 6-oxobornyl acetate, β-thujone, 1-borneol, exo-2hydroxycineole acetate [10].

Octadecyl sorbent was also proved to be the best sorbent for retaining hexanal and hexanol – the compounds responsible for beany flavour of soymilk. Many sorbents were tested considering polarity of hexanol and hexanal reverse-phase sorbents were preferable, but only one adsorbed both mentioned compounds, which were then eluted with methanol [11].

A solid phase extraction on a trifunctional silane SPE C18 cartridge was utilized to evaluate residues of essential oil components in honey. Some of essential oils have been tested successfully against the mite and are applied to control varroosis but the drawback of such a natural treatment is a high level of residues found in honey that may change its taste. Retained compounds such as thymol, menthol, eucalyptol, and camphor were eluted with acetone [12].

An endcapped C18 SPE cartridge and hexane as eluent were used for re-extracting the analytes after subcritical water extraction of essential oils from Thymbra spicata, which were carvacrol and thymol – more than 90%, (E)-car-3-en2-ol and enantiomers of α-pinene. In this work, also the efficiency of the C18 material was tested with steam-distilled sample of essential oil of T. spicata with a known composition, which showed that there were almost no changes in the sample composition after the application of SPE of C18 material [13].

Another cartridge used in the analysis of volatile compounds is a florisol cartridge with MgO/SiO2 phase that enables reversed phase extraction of polycyclic aromatic hydrocarbons. An example of such a use can be a separation of Smyrnium olusatrum stem essential oil from aqueous phase after hydrot/distillation. Three fractions were collected using dichloromethane, dichloromethane–methanol and methanol in turn. As NMR and GC-MS analysis showed, the first fraction was constituted by furanodiene, while the second fraction was constituted by another compound which remained unknown [14].

On-line coupling of solid-phase extraction or liquid chromatography with gas chromatography for the analysis of biological samples reported [15]. Selection of a suitable on-line SPE–GC or LC–GC method
for the analysis of biological samples must take into account the type of sample matrix and the purpose of the analysis.

In the present work solid-phase extraction followed by GC-mass spectrometry and gas chromatography was used to re-extract and determined E-cinnamaldehyde, the main component of Cinnamon bark oil. Thus at first response surface methodology (RSM) was used to optimize the extraction yield and at the highest obtainable extract concentration. The extraction yield was defined as the amount of E-cinnamaldehyde. In this regard, initially aqueous extract from cinnamon (C. zeylanicum) bark as an essential oil-bearing material extracted by superheated water extraction (SWE) technique at different temperatures, flow rates and particle sizes. Then essential oil extracted from aqueous extract by solid phase extraction method and optimized the suitable elution solvent.

2. Material and Methods

2.1. Sample preparation

Cinnamon barks imported bulk from India were taken from the Medicinal Research Laboratory of Iranian Research Organization for Science and Technology (IROST, Tehran, Iran). The moisture content of the bark was 13.4% (dry basis). The samples were stored in polyethylene bags at –70°C until used. The samples were ground within 3 min using a laboratory mill immediately prior to extraction to minimize loss of volatiles. Ground cinnamon barks were sieved into mean particle size from 0.25 to 1.00 mm using ASTM standard sieves within 10 to 15 min.

2.2. Chemicals

Methanol and n-hexane (HPLC grade), ethyl acetate, acetone and ethanol (Aldrich Chemical Co., Milwankee, WI) were used in solid phase extraction (SPE) experiments. E-cinnamaldehyde (Merck, Darmstadt, Germany) was used as authentic component for GC calibration purposes. Doubly distilled water purified through a Milli-Q deionizing unit (Millipore, Bedford, MA) was used as extractant.

2.3 Hydrodistillation

The barks (50.0 g) were ground and extracted using Clevenger type hydrodistillation extractor to yield (v/w, dry basis) 3.6% essential oils (mean of two replications). 200 mL of water for 3 h was used. To be able to compare the results with SWEs and based on density calculation, 0.062 g of essential oil (1:25 dilution ratio) was dissolved in 2 mL n-hexane prior to the GC.

2.4 SWE and SPE systems

SWEs were carried out in a laboratory-built apparatus shown in Fig. 1 Detailed description of the apparatus has been presented elsewhere [16]. It was mainly consists of 5 L de-ionized water feed tank with N₂ gas entering and purging capability (nearly 20 min), a high pressure metering pump (Eldex, Optos series, Model 2S, USA, a cylindrical extraction chamber (103 mm × 16 mm i.d.), and a double pipe heat exchanger (cooling surface area: 240 cm², cooling media: tap water, flow rate: 2 L/min). At the end of each extraction run, 10 mL of the obtained extract was used for SPE and pre-concentration before GC
analysis. For all experiments, 2.0 g of ground cinnamon bark was used at 20 bar pressure to maintain the water as a liquid at the extraction temperatures and the extraction time was set to 120 min.

Before GC analysis essential oil components from *C. zeylanicum* were extracted from SWE extracts using SPE procedure. Solid phase extraction manifold made in our laboratory shown in Fig. 2 four channel device, equipped with Waters Co. vacuum pump. The experiments were carried out using 360 mg cartridge Sep-Pak Classic C18 (Waters Co., UK). In SPE method each cartridge was conditioned by passing 2 mL methanol and 2 mL of water, respectively and dried completely using vacuum. Then, 10 mL of superheated water extract was loaded on it and essential oil components were eluted with 2 mL of elution solvent to 5 mL calibrated flask prior to GC.

![Fig. 1. Schematic diagram of SWE extraction system; BA: balloon; BPR, back pressure regulator; BU: burette; C: N₂ cylinder; EC: extraction cell; HX: heat exchanger; MF, micro filter; NV: needle valve, OV: oven; P: high pressure pump; PI, pressure indicator; TI, temperature indicator; V: ball valves; W: Water Vessel; WI, Water inlet; WO: Water Outlet.](image-url)
2.5 Chromatographic conditions

The extracts were analyzed using a PU-4500 gas chromatograph (Phillips Co., Cambridge, UK) equipped with flame ionization detector and a 25-m PB-1 fused silica column (0.53 mm i.d., 1.0 mm film thickness). The oven temperature program was a 3 °C/min temperature ramp from 55 to 200°C. The carrier gas was helium (99.999%, Roham Gas Co., Tehran, Iran). The column head pressure was 0.27 bar. The detector and injector temperatures were 250 and 240 °C, respectively. External standard solution was E-cinnamaldehyde in methanol: H₂O (70:30) and the concentration range was 50 to 3000 ppm.

GC-mass spectrometry (MS) analysis was conducted on a Varian Saturn model 3400 GC-MS system (Varian Co., Palo Air., CA) equipped with a DB-5 fused silica column (30 m × 0.25 mm, film thickness of 0.25 μm) and interfaced with a Varian ion trap detector. The GC conditions were: oven temperature from 60 to 240 °C at 3 °C/min; injector and transfer line temperature, 250 and 260 °C; carrier gas, helium at a flow rate of 1 mL/min; splitting ratio, 1:60. The detector temperature was maintained at 240 °C. The MS conditions were: ionization energy, 70 eV; mass range, 40–400 amu and scan mode electron impact (EI). The percentage composition of the identified components was calculated from the GC peak area. The components were identified by comparing their retention times and mass spectra with those of pure reference components. Mass spectra were also compared with those in the NIST (National Institute of Standards and Technology), WILEYS and TERPENOIDES mass spectra libraries and our own created library.
2.6 Experimental design

RSM was used to evaluate the effects of extraction temperature (T), superheated water flow rate (F) and mean particle size (D) on the yield of essential oils in terms of E-cinnamaldehyde quantity. The coded and uncoded independent variables used in the RSM design [17] and their respective levels were listed in Table 1.

Table 1. Codes, ranges and levels of independent variables of temperature (T), superheated water flow rate (F) and mean particle size (D) in RSM design

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Independent variables</th>
<th>Coded levels</th>
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<tr>
<td></td>
<td></td>
<td>-1</td>
</tr>
<tr>
<td>X₁</td>
<td>T (°C)</td>
<td>100</td>
</tr>
<tr>
<td>X₂</td>
<td>F (mL/min)</td>
<td>1.0</td>
</tr>
<tr>
<td>X₃</td>
<td>D (mm)</td>
<td>0.250</td>
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</table>

The experimental design was based on the face centered central composite design using 8 cube points, 3 center points in cube and 6 axial points as shown in Table 2.
Table 2. Experimental and predicted data for the yield and extract concentration obtained from the central composite experimental design

<table>
<thead>
<tr>
<th>Run No.</th>
<th>X1</th>
<th>X2</th>
<th>X3</th>
<th>Yield (%), dry basis</th>
<th>Extract concentration (mg/mL)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Experimental</td>
<td>Predicted</td>
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<tr>
<td>1</td>
<td>100</td>
<td>1.0</td>
<td>1.000</td>
<td>1.29</td>
<td>1.42</td>
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<tr>
<td>2</td>
<td>100</td>
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<tr>
<td>3</td>
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<td>4.0</td>
<td>1.000</td>
<td>2.49</td>
<td>2.49</td>
</tr>
<tr>
<td>4</td>
<td>130</td>
<td>2.5</td>
<td>0.625</td>
<td>1.32</td>
<td>1.68</td>
</tr>
<tr>
<td>5</td>
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<td>2.5</td>
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<td>2.51</td>
<td>2.68</td>
</tr>
<tr>
<td>6</td>
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<td>1.000</td>
<td>1.89</td>
<td>1.87</td>
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<tr>
<td>7</td>
<td>130</td>
<td>2.5</td>
<td>0.625</td>
<td>2.12</td>
<td>1.68</td>
</tr>
<tr>
<td>8</td>
<td>160</td>
<td>1.0</td>
<td>0.250</td>
<td>1.45</td>
<td>1.73</td>
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<tr>
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<td>0.625</td>
<td>1.63</td>
<td>1.25</td>
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<td>2.5</td>
<td>0.625</td>
<td>1.43</td>
<td>1.30</td>
</tr>
<tr>
<td>11</td>
<td>130</td>
<td>2.5</td>
<td>0.625</td>
<td>1.65</td>
<td>1.68</td>
</tr>
<tr>
<td>12</td>
<td>100</td>
<td>2.5</td>
<td>0.625</td>
<td>0.83</td>
<td>0.98</td>
</tr>
<tr>
<td>13</td>
<td>130</td>
<td>2.5</td>
<td>0.250</td>
<td>2.26</td>
<td>2.12</td>
</tr>
<tr>
<td>14</td>
<td>100</td>
<td>4.0</td>
<td>0.250</td>
<td>1.89</td>
<td>1.90</td>
</tr>
<tr>
<td>15</td>
<td>130</td>
<td>4.0</td>
<td>0.625</td>
<td>1.75</td>
<td>2.16</td>
</tr>
<tr>
<td>16</td>
<td>100</td>
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<td>2.88</td>
</tr>
<tr>
<td>17</td>
<td>160</td>
<td>4.0</td>
<td>0.250</td>
<td>2.23</td>
<td>2.09</td>
</tr>
</tbody>
</table>

All experimental trials were randomly performed to minimize the effect of unexplained variability in the observed responses due to extraneous factors [18]. Three replicate runs at the center of the design were performed to allow the estimation of pure error. Extraction yield (Y) and extract concentration (C) were considered as the response functions (RE). It means that obtaining the essential oils at the highest value and at the same time, collecting the most concentrated extract is desirable. A second order polynomial equation (1) was used to express the response as a function of the independent variables,

$$RE = \beta_0 + \sum_{i=1}^{2} \beta_i X_i + \sum_{i=1}^{2} \sum_{j=1}^{2} \beta_{ij} X_i^2 + \sum_{i=1}^{2} \sum_{j=1}^{2} \beta_{ij} X_i X_j$$

where RE represents the response variables, $\beta_0$ is a constant, $\beta_i$ the linear coefficient, $\beta_{ij}$ the quadratic coefficient and $\beta_{ij}$ the cross product coefficient. $X_i$ and $X_j$ are levels of the independent variables. The
model was built based on the variables with confidence levels of 95%. The coefficients of the response surface equations were estimated by Minitab Version 15.1.30.

For separation part, in all experiments aqueous solution from superheated water extraction were used to evaluate SPE method for the highest yield of E-cinnamaldehyde essential oils in cinnamon bark. Based on E-cinnamaldehyde solubility in different solvents, a preliminary study for E-cinnamaldehyde extraction by SPE method was performed. Solvents were selected to be methanol: water mixture (at different ratios), n-hexane, ethyl acetate (EA), acetone and ethanol. GC analysis showed in Fig.3 that the highest yield of E-cinnamaldehyde was obtained by methanol: water (60:40) mixture.

![Chromatogram Overlay](image)

Fig. 3. GC overlay for different solvent for SPE extraction: line 5 Mix methanol:H₂O (60:40), line 4 EtOH, Line 3 Mix Hexane: EA, line 2 EA, and line 1 Aceton.

Different ratio of methanol: water 80:20, 70:30, 60:40 (v/v) also studied. GC results showed in Fig. 4 that methanol: water ratio (70:30) (v/v) extracted the highest yield of E-cinnamaldehyde. In the finalized procedure, each cartridge was washed with 2 mL methanol and 2 mL of water, respectively and dried completely using vacuum. Then, 10 mL of superheated water extract was loaded on it and essential oil components were eluted with 2 mL of methanol-water mixture (70:30) to 5 mL calibrated flask. GC analyses were done by external standard method using standard calibration curve.
3. Results and Discussion

3.1 Fitting the model

The predicted values of E-cinnamaldehyde yield and its concentration in the extract were calculated using the regression model and compared with the experimental values, Table 2. The estimated coefficients of the variables in the models are given in Table 3.
The values of the coefficient of determination, R^2, as a measure of the degree of fit, for yield (0.853) and extract concentration (0.946) are both high enough to confirm that the model represents the experimental results adequately. As represented in Table 3, it can be found that the variables with the most significant effect on the yield were the linear and quadratic terms of temperature (p<0.05) and the quadratic term of particle size (p<0.05). It is in accordance with that the extraction temperature is the key factor in SWE process [5].

### 3.2 Optimization of extraction condition

The optimum operating conditions was determined by defining the highest values achievable for the yield and extract concentration. The yield and extract concentration in terms of the main component of cinnamon bark, E-cinnamaldehyde, would be considered optimum with minimum yield of 1.8% and minimum concentration of 0.12 mg/mL as mean values in the whole 17 experiments. The criteria used
for optimization included maximum yield and maximum extract concentration. Considering software generated results for the responses, the optimum combined condition was found to be at 138°C, 1 mL/min and 1 mm. The model prediction capability for optimum response values was verified using generated operating conditions for temperature, flow rate and mean particle sizes. Experimental and predicted values for the yield and extract concentration were 2.69 and 2.21%, and 0.318 and 0.280 mg/mL, respectively. The results show that acceptable agreement exists between values calculated using the model and experimental values.

After preliminary study for SPE extraction, optimum conditions on the basis of highest E-cinnamaldehyde yield determined. As GC results showed nonpolar like n-hexane and midpolar solvent like mix (Hexane: EA) had no good separation for cinnamon bark essential oil. The best extraction obtained by mix methanol and water. Comparison with different ratio of Polar elution solvent (Methanol: H2O) in Fig.4 determined that the amount of extraction were close to each other, but the best one were methanol-water mixture (70:30). For SPE the all separation carried out by washing each cartridge with 2 mL methanol and 2 mL of water, respectively and dried completely using vacuum. Then, 10 mL of superheated water extract was loaded on it and absorbed components were eluted with 2 mL of methanol-water mixture (70:30).

3.3 Comparison with hydrodistillation method

In Table 4, the results of comparison among the SWE and hydrodistillation have been shown. As can be seen, up to 8 components including Z-cinnamaldehyde and E-cinnamaldehyde as the main oxygenated components (C9H8O) and 6 other sesquiterpenes (C15H24) were identified in the samples. These components make up more than 95% of the oil. The mean relative standard deviation per peak was calculated to be 15%.

<table>
<thead>
<tr>
<th>Components</th>
<th>RIa</th>
<th>SWEb</th>
<th>Hydrodistillationc, t</th>
</tr>
</thead>
<tbody>
<tr>
<td>Z-cinnamaldehyde</td>
<td>1216</td>
<td>0.603</td>
<td>0.688</td>
</tr>
<tr>
<td>E-cinnamaldehyde</td>
<td>1278</td>
<td>88.507</td>
<td>79.600</td>
</tr>
<tr>
<td>α-Copaene</td>
<td>1379</td>
<td>8.601</td>
<td>7.234</td>
</tr>
<tr>
<td>E-Caryophyllene</td>
<td>1421</td>
<td>t</td>
<td>0.737</td>
</tr>
<tr>
<td>Germacrene D</td>
<td>1482</td>
<td>t</td>
<td>0.895</td>
</tr>
<tr>
<td>α-Muurelene</td>
<td>1501</td>
<td>t</td>
<td>3.058</td>
</tr>
<tr>
<td>δ-Cadinene</td>
<td>1524</td>
<td>0.668</td>
<td>6.298</td>
</tr>
<tr>
<td>Cubenene</td>
<td>1535</td>
<td>1.620</td>
<td>1.490</td>
</tr>
</tbody>
</table>

a Retention indices on the DB-5 column
b Sample = 2.0 g, Temperature = 138 °C, Flow rate = 1.0 mL/min, Particle size = 1.000 mm, Pressure = 20 bar, Extraction time = 120 min.
c Extraction time = 3 hr,
t = trace < 0.01

The extracts compositions as E-cinnamaldehyde percentage were 88.507% and 79.600% for SWE and hydrodistillation, respectively. It showed that the SWE extract was richer in E-cinnamaldehyde as the main and desirable component of cinnamon bark essential oil. Considering cinnamon bark essential oil density (1.05 g/mL) and E-cinnamaldehyde percentage (79.600%), it may be concluded that the extraction yield based on that component was higher for hydrodistillation (3.00%) than that for the optimized SWE (2.69%). On the other hand, except for α-copaene and cubenene, undesirable non-
oxygenated components like E-caryophyllene, germacrene D, α-muurelene, and δ-cadinene had significantly lower values in the SWE method. It may be the result of low solubility of such sesquiterpenes in water. These facts showed that SWE extracted more valuable oxygenated components selectively.

4. Conclusions

The main essential oils of cinnamon bark were successfully extracted by solid phase extraction method followed by gas chromatography. C18 SPE cartridge and mix methanol:water as eluent were used for re-extracting the essential oils after the superheated water extraction from cinnamon bark. As GC results showed nonpolar and midpolar solvents were not good extractants for cinnamon bark essential oils. The best extraction obtained by polar solvents like mix methanol: water (70:30). Thus results show that SPE is a powerful method for sample separation and it may be useful in this area. The SPE method has been applied as an alternative to liquid-liquid extraction for simplicity, low cost and has many advantages in comparison with more traditional sample preparation techniques. Also, the SWE process was optimized using RSM to extract essential oil components of cinnamon bark and compared with hydrodistillation method.

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