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Comparison of essential oils of clove buds extracted with supercritical carbon dioxide and other three traditional extraction methods

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Abstract

Supercritical fluid extraction (SFE) of essential oil from clove buds with CO_2 was explored. The effect of different parameters, such as temperature (30 °C, 40 °C, 50 °C), pressure(10 MPa, 20 MPa, 30 MPa) and particle size (three degree index), on the extraction yield and the content of eugenol in extracts was investigated using three-level orthogonal array design. The experimental results show that the temperature has the largest effect on the eugenol content of the extracts, and particle size has the maximum effect on the oil yield. The essential oil of 19.56% yield, in which the maximum content of eugenol in extracts is 58.77%, can be extracted from clove buds at pressure of 10 MPa and temperature of 50 °C. Essential oil of clove buds obtained by SFE, hydrodistillation, steam distillation and Soxhlet extraction were further analyzed by gas chromatography/mass spectrometric detection to compare the extraction methods. Twenty three compounds in the clove oils have been identified, showing that the composition of the clove oil extracted by different methods is mostly similar, whereas relative concentration of the identified compounds is apparently different. General characteristics of the clove oils obtained by different methods were further compared, and SFE is considered as the optimum process among the four processes for obtaining clove oil with high quality.

Keywords: Supercritical fluid extraction; Carbon dioxide; Essential oil; Clove bud; Steam distillation; Hydrodistillation; Soxhlet extraction

1. Introduction

Clove (*Eugenia caryophyllata* Thunb.) is widely cultivated in Madagascar, Sri Lanka, Indonesia and the south of China (Bureau of Drug Administration of China, 1989). Clove bud oils have biological activities, such as antibacterial, antifungal, insecticidal and antioxidant properties, and are used traditionally as flavoring agent and antimicrobial material in food (Huang, Ho, Lee, & Yap, 2002; Lee & Shibamoto, 2001; Velluti, Sanchis, Ramos, & Marín, 2003). For example, clove oil was effective against *L. monocytogenes* and *S. Enteritidis* in tryptone soya broth (TSB) and cheese (Smith-Palmer, Stewart, & Fyfe, 1998, 2001). The high levels of eugenol contained in clove essential oil give it strong biological activity and antimicrobial activity. This phenolic compound can denature proteins and reacts with cell membrane phospholipids changing their permeability (Briozzo, 1989; Deans & Ritchie, 1987). Clove oil also has several therapeutic effects, including antiphlogistic, antivomiting, analgesic, antispasmodic, anticarminative, kidney reinforcement, antiseptic, HCMV extracorporeal restraining effect (Liu, Mao, & Hong, 1997; National Pharmacopoeia Committee of China, 2000). In Korea, clove oil has been successfully used for asthma and various allergic disorders by oral administration (Kim, Lee, & Hong, 1998).

The essential oil of aromatic herbs is traditionally obtained by hydrodistillation, steam distillation, or solvent

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extraction. These processes cost not expensive but can induce thermal degradation, hydrolysis and water solubilization of some fragrance constituents. Extracts obtained by solvents contain residues that pollute the foods and fragrances to which they are added. These disadvantages can be avoided by using the supercritical fluid extraction (SFE) process (Mostafa, Yadollah, Fatemeh, & Naader, 2004; Reverchon, 1997). It is well known and SFE has been established as an environmentally benign technique for separating essential oils from the vegetable substrates. Moreover, extracts obtained by SFE can retain the organoleptic characteristics of the starting spice material (Biljana, Zika, Vladimir, & Aleksandar, 2005).

Supercritical CO_2 extraction of cloves oil has been performed previously by some authors (Della Porta, Taddeo, D'Urso, & Reverchon, 1998; Liu, Chen, Chen, & Chang, 2003; Reverchon & Marrone, 1997; Rodrigues et al., 2002). The conditions explored were at pressures from 10 to 50 MPa and temperatures ranging from 30 to 40 °C. Compounds with high molecular weight and coloring materials, such as chlorophyll, were recovered together with the fragrance constituents owing to the high pressures utilized. For example, in the extraction performed by Gopalakrishnan, Shanti, and Narayanan (1990), increasing the extraction pressure from 10 to 50 MPa at a temperature of 40 °C resulted in an increase of the chlorophyll content in the extract (Gopalakrishnan et al., 1990). Comparison of some essential oils obtained by SFE with conventional methods and GC analysis of clove oil in ethanol had been studied by some authors (Myint, Wan, Mohamad, & Kadhum, 1996; Reverchon & Senatore, 1992; Scalia & Giuffreda, 1999), however, none of investigations has examined in detail the comparison of essential oil composition between clove buds oil obtained by SFE and the conventional extraction techniques such as hydrodistillation, steam distillation, and solvent extraction.

Since the clove oil has been used widely as pharmaceuticals, flavoring and antimicrobial agents in food industry, it is necessary to find the most suitable method for the improvement of the quality of clove oil. The aim of this work is to compare clove oils obtained by the supercritical CO_2 extraction with other three traditional methods, in which extraction of clove oil from clove buds with supercritical CO_2 was first investigated intensively. Compositions of clove oil were analyzed by gas chromatography (GC) and gas chromatography–mass spectrometry (GC–MS).

2. Materials and methods

2.1. Materials

The buds of clove (*E. caryophyllata* Thunb.) were purchased from Tianjin factory for Chinese herbs. The samples were dried at 30 °C in a ventilated drying oven and stored in plastic bags at ambient temperature and protected from light. The samples were ground by a FW80 Sample Mill (Taisite CO., Tianjin, China) in different periods to get the different particle distribution, which was measured by mechanical sieving after extraction and calculated by weight of different size of clove bud particle. Grades of particle size was classified on the following scale: $1 > 10$ mesh; $2 = 10$–20 mesh; $3 = 20$–40 mesh; $4 = 40$–60 mesh; $5 = 60$–80 mesh; $6 = 80$–100 mesh; $7 = 100$–120 mesh; $8 < 120$ mesh. Particle size index was calculated by following formula: Particle size index $= \sum$(weight of each grade $\times$ grade)/(total weight $\times$ highest grade). The particle size index of material in this experiment was 0.7944, 0.6430, 0.5223, and named as 1#, 2# and 3#, respectively.

The solvents and chemicals were obtained from following sources: carbon dioxide, 99.99% purity, from Tianjin Anxing gas factory; China. Dichloromethane, purity > 99.9%, from Tianjin chemical Co., China; Eugenol, Purity $\geqslant$ 99.0% (GC), from Fluka Co., Germany; Eugenol acetate, Purity > 90.0% (GC), TCI America Co., Japan.

2.2. Experimental apparatus and methods

2.2.1. Supercritical CO_2 extraction

Extraction of essential oil from clove buds was experimentally determined using the Speed SFE instrument (Applied Separations Inc., Allenton, PA, USA). Liquid CO_2 was pressurized with a high-pressure pump and then charged into the extraction column to desired pressure. The pressure was controlled to an accuracy of about 1% over the measuring range. The extraction column was 32 ml with 14.40 mm inner diameter and 195 mm length, being packed with powdered raw materials and glass beads. The extraction column was heated with an oven and its temperature was indicated and controlled by a thermocouple to within ± 1 °C. The supercritical CO_2 with dissolved compounds passed through a heated micrometer valve, and was subsequently expanded to ambient pressure. The extract was precipitated in a collect vial at ambient pressure and temperature. A calibrated wet-test meter at known temperature and pressure measured the total amount of CO_2.

For each extraction test, the extractor was charged with about 15 g of ground clove bud powder. CO_2 flow rates ranging about 2 l/min were used. The oil weight was measured by precision balance until no oil was extracted out from the clove bud powder.

2.2.2. Hydro and steam distillation

The plant (100 g of dried and ground clove buds) in 500 ml flask was submitted to hydrodistillation for 4–6 h and steam distillation for 8–10 h.

The volatile distillate was collected until no oil drop out. The distillate was saturated with sodium chloride and added with some ether. Then, the ether layer and hydro layer were separated by funnel. After dehydrated by anhydrous sodium sulphate, the ether layer was further heated in 60 °C water bath to make oil to be concentrated and the ether to be recovered. The oil was weighed and refrigerated prior to analysis.