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Ginger (*Zingiber officinale* R.) extracts obtained using supercritical CO_2 and compressed propane: Kinetics and antioxidant activity evaluation

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ABSTRACT

This work reports the extraction of ginger (*Zingiber officinale* Roscoe) roots using sub and supercritical CO_2 and compressed propane as solvents. Antioxidant activity effect and phenolic content were evaluated on the extracts obtained. The extractions were performed in a laboratory scale unit at pressures of 8.0 MPa, 16.5 MPa and 25.0 MPa using CO_2 and 3.0 MPa, 6.5 MPa and 10.0 MPa using propane, and at 293.15 K, 313.15 K and 333.15 K for both solvents. The operating conditions tested achieved a maximum yield of 3.21 wt% for the CO_2 extraction and 2.75 wt% for the extraction using propane as solvent. When CO_2 was used as solvent, the pressure and temperature presented significant effect on the extraction yield. When propane was used, the most important variable was the pressure that presented a positive effect on the extraction yield. The chemical profiles were determined by gas chromatography and were similar for the two solvents, in which the main compounds were α-zingiberene, β-sesquiphellandrene, α-farnesene, geranial, β-bisabolene and β-eudesmol. The antioxidant activity assays were performed on the extracts obtained using the phosphomolybdenum reducing method. The extracts obtained using supercritical CO_2 and compressed propane presented antioxidant effects. The highest antioxidant activity (931.67 ± 2.51 mg of α-tocopherol/g of extract) was found for extracts obtained using supercritical CO_2 as solvent at 313.15 K and 16.5 MPa.

1. Introduction

Ginger (*Zingiber officinale* Roscoe) is a plant that belongs to the Zingiberaceae family and is widely used in food production, in products such as jams, pickles, chutneys, beverages and bakery products, as well as in other industrial sectors. Its rhizome is a common ingredient in folk medicine [1–3]. Ginger rhizomes and their extracts are widely used in popular medicine and there are many studies that confirm their beneficial effects against the symptoms of diseases, acting as an anti-inflammatory, antiemetic, anti-tumor, analgesic, anti-hemorrhagic, neuronal cell protective, anti-rheumatic [4–13], antifungal [1,14] and antibacterial agent [15–19].

Ginger extracts have been identified in many studies as containing a high content of antioxidant compounds [20–26]. The antioxidants are compounds that act as inhibitors of free radical formation by interfering with fundamental oxidation mechanism [27], increasing the shelf-life and useful life of a wide variety of foods. The most commonly applied antioxidants include synthetic phenols, such as, butylated hydroxytoluene (BHT) and butylated hydroxyanisole (BHA). The growing interest in natural foods has increased the demand for antioxidants that can be obtained from natural sources [28,29]. Natural antioxidants are important in the food industry not only because of their utility as a method for preventing oxidation but also because of their beneficial effects on human health [30].

The extract quality is greatly influenced by the extraction methodology used and solvent extraction techniques generally employ high temperatures. Several studies have shown that heat treatment can reduce the antioxidant activity and total phenolic content in the extracts [31–33]. The use of supercritical fluid extraction (SFE) can reduce significantly the problems related to the thermal degradation of the compounds [34] and facilitates the recovery of the solvent due to the volatility of the fluid. Thus extraction processes employing supercritical fluid as solvent represent an interesting and attractive approach [35]. The use of a pressurized fluid (under subcritical conditions) to obtaining extracts is known to be a fast and efficient method for the extraction of non-polar compounds from vegetal sources. Supercritical or pressurized solvents are of particular interest since their physicochemical properties (density, diffusivity, viscosity, and dielectric constant) can be tuned by altering the pressure and temperature, allowing control

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of the solvating power and selectivity of the solvent during the extraction process [34].

Roy et al. [35] studied the effects of the solvent flow rate, particle size distribution, temperature (288–353 K) and pressure (8.0–30.0 MPa) on the kinetics of the extraction of ginger with supercritical CO_2. At 24.5 MPa the mass transfer rate increased with increasing temperature, while at 10.8 MPa it decreased. Zancan et al. [36] observed that the rate of mass transfer and yield increased with a decrease in the density of CO_2 and these authors observed that the overall efficiency of the process was increased following a temperature increase from 298 K to 303 K.

Norulaini et al. [37] evaluated the effect of different combinations of temperature, pressure and CO_2 mass on the ginger extraction yield and observed that the interaction between pressure and temperature reduces the yield and the interaction between temperature and CO_2 mass presented a positive effect on the extraction yield. The combination of low pressure and low temperatures led to lower yields, while high pressure (50 MPa) and low temperatures (303–313 K) enhanced the extraction yield.

Monteiro [38] studied the extraction of the essential oil/oleoresin of ginger (*Z. officinale* Roscoe) with supercritical CO_2, in order to evaluate the influence of temperature, particle size and extraction time on the overall yield and chemical composition of the volatile oil/ginger oleoresin. The results obtained by Monteiro [38] showed that the highest and lowest yields were obtained when the average fractions (dried at 303 K/60 min) and the mixture of all fractions were used, respectively. The author also evaluated the effects of the process variables of pressure (7.0–25.0 MPa) and temperature (289–313 K) on the mass transfer rate during the extraction and on the oleoresin yield obtained during the period in which a constant extraction rate was observed. The statistical analysis conducted by these authors showed that the effect of pressure was predominant in the process.

Besides CO_2, several fluids can be applied under subcritical and supercritical conditions. However, CO_2 is the solvent most widely used to obtain natural extracts due to their thermodynamic and physicochemical properties. This solvent, besides having a critical point under relatively mild conditions and being of low cost, is readily available, nontoxic, nonflammable, easily removed from the extracted material and environmentally friendly [39,40]. In addition, when supercritical CO_2 is used as a solvent in the extraction of thermolabile compounds, particularly antioxidant compounds, the antioxidant activity of these compounds is relatively high, when compared with organic solvents [41–43]. This is because in the conventional process, employing an organic solvent, the oxidation of the compounds occurs during the solvent recovery.

Besides CO_2, some studies have shown that subcritical propane can be used for the extraction of natural products with interesting results [44–48]. Although propane does not offer many of the qualities associated with CO_2, under certain conditions it might represent a better solvent for the extraction of oils and natural products. Propane is relatively inexpensive, has a high solvation power, does not leave toxic residues and with its use the extraction requires low pressures in comparison with supercritical CO_2 [49]. From an economic standpoint, processes carried out at low pressures and temperatures can reduce the extraction costs and provide high yields in a shorter time, thus it is possible to optimize the process by ascertaining the optimum conditions [44,45,47,48,50,51].

However, information regarding comparisons between extraction processes employing supercritical CO_2 and compressed propane are still scarce in the literature. Aspects related to the extraction kinetics and the chemical composition of the extracts are extremely important to clarifying our understanding of the phenomena involved in the process of extraction with pressurized fluids. Although several studies which evaluate the antioxidant activity of ginger extracts can be found in the literature, those obtained with the use of CO_2 as the solvent have not been extensively investigated and there are no studies on ginger extracts obtained using propane. In this context, the focus of this study was to compare the ginger extraction processes using CO_2 and propane as solvents. The effects of the solvent and the extraction process variables (pressure and temperature) on the chemical composition, antioxidant activity and total phenolic content of the ginger extract obtained using supercritical CO_2 and compressed propane is also subject of this work.

2. Materials and methods

2.1. Sample preparation

Ginger rhizomes (*Zingiber officinalle* Roscoe) were acquired from a local producer in Morretes (Paraná, Brazil). The rhizomes were washed and sanitized and then stored at 255.15 ± 2 K in polypropylene plastic bags (1 kg) to protect rhizomes against the action of microorganisms and slow down the biochemical reactions. The samples were cut into gingerbread oarlocks, and dried in an air circulation oven at 303.15 ± 2 K [36], until reaching a moisture content of 10.8%. The dried ginger was packed in polypropylene plastic bags (1 kg) and kept in a freezer at 268.15 ± 2 K. Immediately prior to extraction, the dried ginger samples were milled in a knife mill and separated using Tyler series sieves with different openings, with the help of a mechanical stirrer (Produtest, São Paulo, Brazil). The average particle diameter was estimated using the method presented by Gomide [52] considering the mass fractions of milled material weighted in the sieves as follows: 12 mesh (25 wt%), 14 mesh (10 wt%), 20 mesh (25 wt%), 28 mesh (25 wt%) and 48 mesh (15 wt%).

2.2. Determination of moisture content and the particle density

The moisture content (H) of the ginger was measured by the toluene distillation method according to AOCS [53], which can distinguish water from volatile material. The values were calculated as follows:

$$H = \left(\frac{V_{H_2O} \cdot \rho_{H_2O}}{w_{sample}} \right) \times 100 \quad (1)$$

where V_{H_2O} is the measured volume of aqueous phase, ρ_{H_2O} is the water density and w_{sample} is the sample mass.

The real density of the milled ginger was measured using a helium pycnometer at the Institute of Chemistry/Unicamp, Campinas, Brazil.

2.3. Classical extraction

The ether extract content was determined in triplicate runs by Soxhlet (Nova Etica, Brazil) extraction using petroleum ether at 60 °C for 6 h, followed by solvent removal at 40 °C. Approximately 5 g of dried ginger was extracted in Soxhlet for 6 h according to a method adapted from AOAC [54].

2.4. Supercritical fluid extraction procedures

The extraction experiments were performed in a home-made laboratory scale supercritical extraction unit (0.08 m^3 inner volume, $L = 0.16$ m, $\phi = 2.52 \times 10^{-2}$ m). The ginger extractions were carried out in a batch extractor with controlled temperature and pressure. The system consists of a jacketed-extractor for temperature control, an ultrathermostatized bath, a needle valve for flow control in the extractor, a syringe-type pump, and pressure and temperature sensors and transducers. For the supercritical and