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Extraction of inflorescences of *Musa paradisiaca* L. using supercritical CO_2 and compressed propane

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ABSTRACT

This work aimed to investigate the extraction of inflorescences of *Musa paradisiaca* L. using supercritical CO_2 and compressed propane as solvents. The extractions were performed in a laboratory scale unit at temperature and pressure range of 313.15–353.15 K and 15–25 MPa for carbon dioxide and 308.15–338.15 K and 3–10 MPa for propane extractions, respectively. A 2^2 factorial experimental design with three replicates at central point was adopted to organize the data collection. The highest extraction yields were 3.60 wt% using $scCO_2$ at 313.15 K and 25 MPa and 3.14 wt% with compressed propane at 338.15 K and 10 MPa. The overall extraction curves were modeled using a model based on the BET theory of adsorption. The kinetic model allowed correlating the different conditions of extraction with both $scCO_2$ and compressed propane. The pressure of $scCO_2$ presented a positive effect on the extraction yield of *M. paradisiaca* L. while temperature presented a negative effect. On the other hand, the increase of temperature allowed higher extraction yields of *M. paradisiaca* L. when propane was used. The most volatile fraction from the $scCO_2$ extracts were composed by lupenone, methyl 2-hydroxy-2-(3-nitrophenyl)-2-(4-nitrophenyl)-acetate, pentacosane, 3,6,9-nonacosatriene, 10-hentriacontene and, 7,23-dimethyltritriacontane while for compressed propane extracts lupenone and 7,23-dimethyltritriacontane were the major constituents.

1. Introduction

Musa paradisiaca L. commonly known as banana belongs to the Musaceae family and has great economic interest due to its worldwide consumed fruits [1]. Additionally, all parts of banana plant (fruits, leaves, peels, root, and, stalks) are used in folk medicine to treat diarrhea, dysentery, and intestinal colitis [2], antilithic [3], inflammation, pain and, snakebite [4–6] and protein metabolic disorders [7]. Furthermore, several pharmacological activities have been reported for this plant such as antimicrobial [8], antiulcerogenic [9], antihelmintic [10], hypoglycemic [11–13], antioxidant [14,15] and hypocholesterolaemic [16] activities.

The inflorescences have been used by the Xokleng Indians (native people from Ibirama, State of Santa Catarina, Brazil) in the formulation of syrup with hot water and honey which is used as an expectorant to treat respiratory diseases [17]. A study indicated the use of hydroalcoholic extracts of inflorescences of *M. paradisiaca* L. with *in vivo* and *in vitro* antioxidant and anti-inflammatory properties, for the treatment of respiratory diseases [18]. Another recent study showed that the hydroalcoholic extracts of *M. paradisiaca* L. inflorescences presented potent *in vivo* anti-hyperglycemic activity and moderate *in vitro* antimicrobial activity against fungi and bacteria [19].

The choice of extracts of natural extraction method is highly recommended for pharmacological or alimentary purposes. In spite of that, extraction methods such as, steam distillation, vacuum distillation, the hydrodistillation, extraction with organic solvents are the techniques most used for obtaining natural products. However, these methods require a high-energy cost and may degrade thermally sensitive substances because of the use of high temperatures for the extraction or separation of the solute-solvent [20]. An alternative method to the conventional solvent-based extractions is the use of supercritical fluid extraction (SFE) or compressed gases (gases at sub critical conditions) as solvents. This method has a number of advantages over other techniques. It is a flexible process due to the possibility of continuous modulation of the solvent

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power to the selectivity of the supercritical fluid (SCF); it avoids the use of polluting organic solvents and expensive post-processing steps for solvent elimination and; it reduces thermal degradation. In addition, the decomposition of thermolabile compounds can be avoided with operation at low temperatures while the absence of light and oxygen prevents oxidation reactions [21,22].

Application of compressed propane as solvent has gained attention due to some advantages and potentials of this type of natural plants extraction. Compressed propane has some advantages over other solvents, as supercritical CO_2 ($scCO_2$), because the former requires lower pressures and provides higher solubility of nonpolar compounds. Studies suggest that propane can be more effective for obtaining natural extracts when compared to $scCO_2$ in relation to the rate and efficiency of the process [23–27].

The studies of alternative methods to extract bioactive compounds of *M. paradisiaca* L. are justified due to the vast representation of the cultivated area of this plant in Brazil, its economic importance, the use of its inflorescences in folk medicine in many countries and the need for deeper knowledge about the properties and composition of its medicinal extracts.

This research was focused on the extraction of *M. paradisiaca* L. inflorescences using $scCO_2$ and compressed propane as solvents. Extraction yields and kinetics of the extraction are reported. The effects of the solvent and the extraction process variables (pressure and temperature) were also investigated. The chemical composition of the extracts obtained with both solvents was determined.

2. Material and methods

2.1. Sample preparation

The inflorescences of *M. paradisiaca* L. were collected in Pinhão (State of Paraná, Brazil). The inflorescences were dried in an air circulation oven at 303.15 ± 2.0 K for 48 h [28]. The dried inflorescences samples were ground in a food chopper and separated using several different Tyler series sieves with a mechanical stirrer (Produtest, São Paulo State, Brazil). Average particle diameter was estimated using the method described by Gomide [29] considering the mass fractions of milled material retained in the following sieves: 12 mesh (23.5 wt%), 16 mesh (23.5 wt%), 32 mesh (34.5 wt%) and 48 mesh (18.5 wt%). Moisture content (H) in the raw material and dried samples of inflorescences of *M. paradisiaca* L. was measured by the toluene distillation method according to AOCS [30], which can distinguish water from volatile material. The moisture values were calculated following equation:

$$H = \left(\frac{VH_2O \times \rho H_2O}{w_{sample}} \right) \quad (1)$$

where VH_2O is the aqueous phase volume (mL), ρH_2O is the water density (g mL^{-1}) and $w_{sample}$is the sample mass (g).

2.2. Classical extraction

The ether soluble content of the extracts was determined in triplicate by Soxhlet (Nova Etica, Brazil) extraction using petroleum ether at 333.15 K for 6 h, followed by solvent removal at 313.15 K. Approximately 3 g of dried inflorescences were used for the Soxhlet extraction which was carried out according to a method adapted from AOAC [31].

2.3. Supercritical fluid extraction procedures

The extractions were performed in a laboratory scale unit based on the apparatus and procedure previously presented by Mesomo et al. [28]. The equipment is composed by a high-pressure jacketed-vessel (7.98×10^{-5} m^3 inner volume, L = 0.16 m and $\phi = 2.52 \times 10^{-2}$ m) coupled to a circulation bath, a micrometering needle valve to control the flow inside the extractor, a syringe-type pump (ISCO, model 500D, Lincoln, NE 68504, USA), and pressure and temperature sensors and transducers (Fig. 1). For the supercritical and subcritical extraction, CO_2 (White Martins S.A., 99.5% purity in the liquid phase) and propane (White Martins S.A., 99.5% purity in the liquid phase) were used as solvents. The extractions were performed with a constant flow rate of 2.0 ± 0.3 cm^3 min^{-1} for both fluids used. In order to determine the influence of the two main factors, temperature and pressure, a randomized 2^2 experimental design with a triplicate center point was used. For all Runs, the extractor was charged with approximately 20.0 ± 0.2 g of dried and milled inflorescences, with a moisture content of 8.50 ± 0.51 wt%, forming a fixed bed. The experiments were performed at temperatures of 313.15, 333.15 and 353.15 K and pressures of 15.0, 20.0 and 25.0 MPa for the extraction using CO_2, and 308.15, 323.15 and 338.15 K and 3.0, 6.5 and 10.0 MPa for propane. After reaching the corresponding sub or supercritical fluid conditions within the extraction, the static time was provided for extraction in order to assure the total solvent penetration into the systems. According to the preliminary test (results not shown) for this raw material a time of 90 min was used. The kinetic of the extraction processes was evaluated by collecting and weighing the extract samples in amber flasks (environmentally cooled at around 298.15 K) at intervals of 10 min with a total extraction time of 180 min. The extracts were gravimetrically quantified at the end of each Run (after 180 min).

2.4. Fixed bed extraction modeling

The modeling used in this work was based on the model proposed and presented by Pardo et al. [32], based on the theory of Brunauer-Emmett-Teller (BET) adsorption, with some differences and considerations.

Based on the general model for the supercritical fluid (SCF) extraction of a solid substrate in a packed bed [32,33], the material balance for the solute in the SCF around a differential element along the axial direction of the extractor can be written as:

$$\frac{\partial C}{\partial t} + u\varepsilon \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2} + \frac{(1-\varepsilon)}{\varepsilon} a_s k_f (C^* - C) \quad (2)$$

where C is the concentration of the solute in the bulk phase, u is the interstitial velocity of the solvent, ε is the void fraction of the bed, D is the axial dispersion coefficient of the solute in the fluid phase, a_s is the effective solid-fluid contact area for mass transfer, $k_f$is the mass transfer coefficient for transport of the solute through the external fluid film around the solid particles and C^* is the concentration of solute in the fluid-phase film that is in equilibrium with the solid surface. As detailed by Pardo et al. [32], this well-known balance equation (Eq. (2)) can be simplified according to the criteria presented by Carberry and Wendel [34] which states that if the length of the reactor/extractor is of at least 50 times the average of particle diameter and the Reynolds number is greater than 10, the term that represents solute accumulation in the bulk phase is negligible when compared to the amount of solute in the solid material [32]. Furthermore, the mathematical model proposed considers the following hypotheses: isothermal and isobaric process along the entire extractor, negligible axial dispersion inside the extractor, the process sharply reaches the equilibrium conditions, the extract is treated as a pseudo-component, and the model is unidimensional and only the axial coordinate is considered. Thus, the mass balance