Simultaneous extraction of sunflower oil and active compounds from olive leaves using pressurized propane

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Abstract

Sunflower is grown in different parts of the world and oil from the grain has many uses, including cosmetics and food. Olive leaves are rich in active compounds with potential for industrial use. The simultaneous extraction of raw materials is an economical and sustainable way of using the same extraction process to obtain products with high added value. The aim of this work was to promote the incorporation of bioactive compounds from olive leaves in sunflower oil by two extraction techniques: pressurized propane (PRO) and Soxhlet (SOX) and to evaluate the increase in oxidative stability and antioxidant activity of oils. The techniques used were useful in producing sunflower oil incorporating olive leaf extract (SFO + OLE); 4.3% 1-octacosanol and 5.8% 1-triacontanol were incorporated, and β-sitosterol increased by at least 90%. Also, SFO + OLE showed an increase in the induction time of 2.7 and 3.7 h compared to SFO for the PRO and SOX methods, respectively. The profile of fatty acids was maintained, with the majority in all samples being oleic and linoleic acids. Consequently, with this procedure it is possible to produce SFO + OLE with better antioxidant activity and better nutritional characteristics using PRO and SOX. The scaled-up of the simultaneous extraction process via pressurized propane is economically viable according to the process simulation and economic evaluation.

Keywords:
Helianthus annuus
Olea europaea
Phytosterols
Pressurized fluid
Oxidative stability
Economic evaluation

Practical Applications: This research has scientific relevance. It shows that sunflower oil is improved by incorporating active compounds from olive leaves, both by the conventional method of extraction and by the technique with pressurized propane. The use of clean technology to increase the nutraceutical content of products is necessary for the agri-food industry. Extraction with pressurized propane has become one of the most promising forms of technology for obtaining lipids and, at the same time, incorporates active compounds that provide a highly competitive potential to the final product. This research shows that olive leaves and sunflower seeds can be combined in the extractor in a structured bed, increasing the active compounds and essential fatty acids in the final product.

1. Introduction

The sunflower (Helianthus annuus L.) is an agricultural crop of great importance in the international market. It is one of the four most crucial oilseed crops globally (along with palm, soy, and rape). Around 90% of the sunflower grain oil (SFO) produced is for human consumption and almost 10% is used for biodiesel production and industrial applications (Martínez-Force et al., 2015). A projection of this scenario predicts that the production of sunflower grains will grow by at least 20% by 2050 (Dominguez Brando and Sarquis, 2012). Sunflower grains contain approximately 55% oil, which can vary according to several environmental factors such as the soil, climate, variety, and other cultivation factors (Sagiroglu and Arabaci, 2005).

About 90% of the fatty acids (FAs) present in SFO are unsaturated, and oleic and linoleic acids represent most of the FAs (Nimet et al., 2011; Pérez-Vich et al., 1998). The high concentration of α-tocopherol compared to other vegetable oils is advantageous (Martínez-Force et al., 2015; Ribeiro et al., 2015). Among its health benefits, SFO also induces a decrease in plasma lipoprotein total cholesterol, i.e., its ingestion avoids...
one of the main factors that cause arteriosclerosis.

During the processing of SFO and other oils of plant origin, lipid oxidation is considered one of the most critical factors affecting its quality attributes, polyunsaturated fatty acids (PUFAs) being the saturated fatty acids (SFA) most sensitive to factors such as temperature and oxygenation. Such deterioration reduces the oil’s service life (da Silva and Jorge, 2012; Yang et al., 2016). This process is harmful to humans due to undesirable changes in oil characteristics (Malheiro et al., 2013). Synthetic antioxidants such as butylhydroxyanisole (BHA), butylated hydroxytoluene (BHT), tert-butylhydroquinone (TBHQ), and propyl gallate (PG) are used to prolong the shelf life of the product (Durán and Padilla, 1993). However, research shows that these compounds are toxic and carcinogenic when consumed frequently (Botterweck et al., 2000; Lanigan and Yamarik, 2002; Saito et al., 2003).

Due to its composition, the sunflower oil presents nutraceutical and therapeutic potential that are emphasized with the increase of other bioactive compounds and improvement in its antioxidant activity (Martínez-Force et al., 2015; Muhammad Anjum et al., 2012). Then, active plant compounds can be used as natural antioxidants in vegetable oils, promoting a reduction in the use of toxic compounds for health reasons (Chiou et al., 2009; Jaski et al., 2019a,b; Jimenez et al., 2011). For example, the use of plant phytosterols in the development of functional foods containing physiologically active components is reported in the literature (Herrero et al., 2011; Xavier and Mercadante, 2019). Consequently, it is important to quest new plant sources that can add quality to the oils and minimize the use of synthetic substances.

Examples of active compounds important for incorporation into foods are phytosterols, which in plants are structural components that stabilize biological membranes and also serve as precursors in the synthesis of essential compounds (Moreau et al., 2002; 2018a). When consumed, phytosterols can lower LDL cholesterol. Consequently, there has been a significant increase in the emergence of functional foods enriched with phytosterols in recent years (Moreau et al., 2018a). Due to the various benefits that phytosterols bring to the body when ingested, foods enriched with phytosterols are increasingly developed and intended by the food industry (Scholz et al., 2015). Among the advantages of ingesting phytosterols, there is a lower risk of diseases such as esophageal cancer (Ramprasad and Awad, 2015; Shahzad et al., 2017).

The active compound octacosanol is a primary aliphatic alcohol and the main component of wax extracted from plant leaves (Taylor et al., 2003). Octacosanol is one of the main constituents of policosanol, a mixture of long-chain aliphatic alcohols (20–36 carbons) formed in addition to octacosanol (C28), triacotanol (C30), hexacosanol (C26), and heptacosanol (C27) (Fernández-Arche et al., 2009). Policosanol shows efficiency in reducing LDL and increasing HDL (Gong et al., 2018).

Also, Olive leaf extract (OLE) has been studied for its high capacity to promote the enrichment of vegetable oils, increasing their shelf life (Jaski et al., 2019a,b; Jimenez et al., 2011). However, there is no evidence from studies that assessed olive leaf active compounds being incorporated into SFO to promote more significant antioxidant activity and resistance to oxidation. Besides that, there are techniques to be explored for this incorporation, such as the use of pressurized propane. These technologies are exploited to improve agro-industrial products (Gullón et al., 2018; Herrero et al., 2011; Souilem et al., 2017).

Conventional extraction techniques, such as the Soxhlet method, and alternative techniques, such as extraction with pressurized fluids, are commonly used to obtain vegetable oils and plant extracts. Conventional extraction generally uses toxic organic solvents (such as methanol, hexane, and chloroform) that leave residues which can damage the health of the consumer, in addition to causing environmental concerns during their disposal. Pressurized fluid extraction techniques are considered more efficient and less aggressive to the environment and are gradually replacing conventional methods (Knez et al., 2019). In this way, ecologically cleaner extractions often use supercritical and subcritical conditions. The high selectivity, absence of light and oxygen, and use of lower temperatures, which avoids the degradation of thermolabile compounds, are the advantages of these techniques that result in high-quality extracts. Also, in these extraction methods, solvents are easily removed from the extract, and the extraction process is faster than the conventional one (Correia et al., 2016; Cuco et al., 2019a, b; C. M. da Silva et al., 2018; R. P. F. da Silva et al., 2016; Knez et al., 2019).

Extractions under pressurized conditions are also associated with a reduction in energy consumption and increased solvent efficiency when elimination of post-processing steps are achieved. The high solubility of propane in vegetable oils makes it widely used for obtaining oils. The results obtained are effective, using a small amount of solvent in a shorter time than carbon dioxide (CO2), which is the solvent most commonly used among pressurized fluids (Ahangari and Sargolzaei, 2012; Knez et al., 2019; Pederssetti et al., 2011; Zanqui et al., 2014).

N-propane is a gas that does not leave any residue in food, and this is one of its advantages for use in the extraction of natural products. As a gas, propane evaporates quickly and does not remain in the oil obtained after extraction. Propane is a safer gas for obtaining residue-free oils, and for this reason, it is being widely studied as an alternative green solvent for obtaining natural and edible products (Chemat et al., 2019; Knez Hrinčić et al., 2018; Oliveira et al., 2021). Due to the potential for exploiting OLE, the high quality of SFO, and the scarcity of studies in the literature on the use of OLE to incorporate bioactive compounds during the extraction process, obtaining a high value-added product is the intention of this study. Such combination of two high-quality vegetable matrices in the same extraction process aims to incorporate active ole compounds in SFO, consequently an increase its oxidative stability and antioxidant capacity is also expected. Therefore, the open literature reports several processes for extracting bioactive compounds from olive leaves using a variety of solvents. The extraction using edible vegetable oils as co-solvent in a pressurized medium with n-propane, solvent, is innovative.

In this context, this work aimed to obtain sunflower oil with improved levels of active compounds, nutritional properties, and oxidative stability, using a combination of sunflower grains and olive leaves in the extraction process. The oil and extract yield, fatty acids profile, content of active compounds, antioxidant activity, and oxidative stability were determined and statistically analyzed. Next, results and insights of the experimental analyses are used to simulate a scaled-up extraction process aiming to assess the economic perspective of the investigated scenario.

2. Materials & methods

2.1. Materials

Peeled sunflower grains and dehydrated olive leaves were the two vegetable matrices used in the extractions. Sunflower grains were purchased at a store specializing in natural products in Maringá, Paraná, Brazil (November 2019 crop). Olive leaves of three varieties (Arbequina, Koroneiki, and Arbosana), cultivated commercially at high altitude in the Brazilian state of São Paulo (22° 00’ 48.6” S, 46° 37’ 59.4” W) were pruned for use in this research. Mid-December was the time chosen for collecting the leaves, before harvesting the fruits, which takes place between February and March in this region of Brazil. This moment was chosen due to previous studies carried out by the local research group and reports in the literature, which showed that there is greater production of active compounds before harvesting the fruits (Alowaish et al., 2018).

N-propane gas (Messer, purity 99.5%) and n-hexane liquid (Sinth, purity 99.9%) were used in the extractions. Helium (White Martins, purity >99%), BFs (Sigma-Aldrich, > 99% purity), Methanol (Panreac, purity 99.9%), Heptane (Anidrol, > 99% purity), N,O-bis(trimethylsilyl) tri-fluoroacetamide trimethylchlorosilane (BSTFA/TMCS, Sigma-Aldrich, > 99% purity) and 5α-cholestanol standard (Sigma-Aldrich, > 99% purity) were used for the analysis of active compounds and fatty acids.

The chemicals, DPPH (1,1-diphenyl-2-picrylhydrazine) (Sigma-
Aldrich, purity ≥90%), ABTS⁺⁺ [2,2-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid)] (Sigma-Aldrich, ≥ 98% purity), Trolox (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid, Sigma-Aldrich, 97% purity), methanol (Panreac, 99.9% purity), ethanol (Anidrol, 99.5% purity) and potassium persulfate (0.140 mol L⁻¹) (Anidrol, > 99% purity) were used for the antioxidant analyses.

### 2.2. Methods

#### 2.2.1. Samples preparation

Grinding of the sunflower grains was carried out in a manual household mill (size < 2.0 mm). The olive leaves were dried in a forced ventilation oven (model 400/4°, Ethik Technology, Vargem Grande Paulista, SP, Brazil) at 35°C for 36 h to reduce the moisture content from 60% to approximately 5%. The dried leaves were ground with a rotary knife cutter (model SL-30, Solab, Piracicaba, SP, Brazil) with granulometry ≤2.0 mm and homogenized. Then the samples were destined for intensification of the extraction process was carried out by clean extraction, via pressurized propane, and classic extraction, via the Soxhlet method.

#### 2.2.2. Extraction with compressed propane

Extractions with propane were performed, in duplicate, in the same household mill (size <2.0 mm). The olive leaves were added first and then the sunflower grains, in a 1 : 3 (w/w) ratio, totalizing ~ 60 g of sample in the extractor (165.2 cm³).

When pressurized, propane first interacts with the grains, extracting the oil, which in turn acts as a co-solvent in this process, extracting the compounds of interest from the olive leaves. This strategy has shown efficiency in recent studies (Cusco et al., 2019a,b; Zanqui et al., 2021).

The experiments were conducted at temperature and pressure of 60°C and 12 MPa, respectively, which favors a higher yield of SFO, as shown in previous studies (Nimet et al., 2011). The time taken for extraction was 60 min at a constant flow rate of 1.5 mL min⁻¹, as described by Trentini et al. (2017).

Propane was pumped and pressurized using a syringe pump (Teledyne ISCO 500D) in the extraction vessel loaded with the samples. The entire extraction procedure was performed in the absence of light. An amber glass bottle was used to collect the extracted oil, and the oil mass was determined at 5 min intervals. Likewise, the mass percentage yield of OLE was determined. The ratio of extracted oil mass to grain mass was used to determine the percentage yield by mass (Eq (1)).

\[
Y (%) = \left(1 - \frac{M}{Gr}\right) \times 100
\]  

where \(Y\) is the percentage mass yield, \(M\) is the mass of oil accumulated in the extraction in grams and \(Gr\) is the mass of grains or leaves used in the extraction in grams.

#### 2.2.3. Kinetic modeling

The mathematical model proposed by Sovová et al. (1994) was used to describe the kinetic data for the pressurized propane extraction of SFO and SFO + OLE. The model addresses two distinct structures in the matrices: one related to the cells that had their walls broken during the milling process, the oil contained in these being considered easy to access by the solvent, and the other to intact cells (i.e., difficult-to-access oil).

The mass transfer of easily accessible oil extraction occurs by convection. In contrast, due to the difficult of interacting to the oil from the intact cells, the mass transfer occurs by intraparticle diffusion. With these characteristics, the extraction curves present three distinct stages, based on the different mechanisms of mass transfer. In the first period, with a constant extraction rate, the easily accessible solute is quickly extracted due to convective mass transfer; in the second period, of falling extraction rate, the mass transfer of the difficult-to-access oil begins by a diffusion mechanism due to the reduction of oil from broken cells, and both mechanisms co-occur; in the last period, diffusion-controlled extraction, only the solute contained in the intact cells is available for extraction, so the mass transfer rate is low and limited by intraparticle diffusion (Fornari and Stateva, 2015).

The model equations for the accumulated mass of extracted oil (\(m\)) as a function of time (\(t\)) in the three different periods are:

\[
m(t) = \begin{cases} 
Y_0t & \text{if } t < t_{CER} \\
Y_0t - k_{a}m_{r}\left(1 - \frac{m_{r}}{m_{f}}\right) & \text{if } t_{CER} \leq t \leq t_{FER} \\
Y_0t - k_{a}m_{r}\left(1 - \frac{m_{r}}{m_{f}}\right) - Z & \text{if } t > t_{FER}
\end{cases}
\]  

where \(t_{CER}\) is the time (min) at which extraction of the oil from the inside of intact particles starts (min), and \(t_{FER}\) is the time (min) at which extraction of easily accessible oil ends. \(t_{CER}\) and \(t_{FER}\) are given by:

\[
t_{CER} = \frac{(1 - r) m_{r}X_{0}}{Y_{S}Z m_{f}}\]  

\[
t_{FER} = t_{CER} + \frac{m_{r}s}{W m_{f}} \ln\left(1 + (1 - r)\frac{W X_{0}}{Y_{S}}\right)
\]  

\[
Z, W, \text{ and } r \text{ (hardly accessible oil fraction) are dimensionless model parameters.} \quad Z \text{ and } W \text{ are defined as:}
\]

\[
Z = k_{f} m_{r s} / m_{f} (1 - \epsilon) \rho_{S}
\]

\[
W = m_{f} k_{a} m_{r} / m_{f} (1 - \epsilon)
\]  

where \(m_{f}\) is the CO₂ mass flow rate (g min⁻¹); \(Y_{S}\) is the apparent oil solubility in supercritical CO₂ solvent (\(\delta_{oil} \rho_{oil}\)) calculated as the ratio of the initial oil mass in the raw material and the oil-free seed feed; \(m_{r}\) is the mass of oil-free seed feed; \(m_{r s}\) is the initial concentration of the extractable solute in the solid matrix (\(\delta_{oil} \rho_{oil}\)), \(\rho_{S}\) is solid density (g cm⁻³), \(k_{a}\) is the volumetric mass transfer coefficients in the solvent and solid phases (min⁻¹), obtained from \(Z\) and \(W\) model parameters.

Agreement between the experimental and model values was evaluated by the average absolute relative deviation (AARD), calculated from Eq. (6).
\[
AARD(\%) = 100 \left( \frac{m_{\text{exp}}^{ij} - m_{\text{calc}}^{ij}}{m_{\text{exp}}^{ij}} \right) \quad (7)
\]

where \(N\) is the number of experimental data points on the kinetic curve, \(m_{\text{exp}}^{ij}\) is the experimental mass of oil, and \(m_{\text{calc}}^{ij}\) is the mass of the oil calculated by the Sovová model, both at point \(j\).

### 2.2.4. Soxhlet extraction

The classic extraction was performed in Soxhlet equipment (Marconi MA 491, Brazil) in duplicate. The extraction of SFO was carried out with 10 g of ground sunflower seeds, without peel, put into filter paper envelopes. Olive leaves already dried and ground, in the same way, were weighed (10 g) and added to filter paper envelopes to obtain the extract (OLE). In the simultaneous extraction, the grains were in the basal part and the leaves in the upper part of the filter paper envelope, in the proportion 1:3 (w/w), totaling 10 g in all. The solvent used was n-hexane to a normal boiling point for 8 h. Removal of solvent from the samples was carried out in an air circulation oven (model 400/4, Ethik Technology, Vargem Grande Paulista, SP, Brazil) at a temperature of 70 °C. Standard rules were used as the basis for this extraction process (AOAC, 2004).

### 2.2.5. Active compounds and fatty acids

The active compounds (phytosterols and tocopherols) and FAs present in the oils and extracts were analyzed on a gas chromatograph coupled to a mass spectrometer (Shimadzu, GC-MS QP2010 SE) equipped with an automatic injector (AOC-20i). Helium was used as the carrier gas at a flow rate of 1.0 mL min \(^{-1}\) with a split ratio of 1: 40 and an injection volume of 2 \(\mu L\). The injection temperature and the GC-MS interface temperature were maintained at 250 and 280 °C, respectively, for analysis of FAs and active compounds. The temperature of the ionic source was 260 °C for both analyses. Mass spectra were recorded at 70 eV with a range of m/z 50 to 550. Compound identification was performed from the library databases NIST14.lbd and NIST14.lbb.

The FA composition was determined after saponification of the samples and derivatization with BF\(_3\) (14% in methanol) for methylation of the FAs following the procedure described by Gonzalez et al. (2013). Heptane was used for sample dilution. A ZB-Wax™ capillary column (Zebron, 30 m \(\times\) 0.25 mm \(\times\) 0.25 \(\mu m\)) was used, and the oven temperature was set at 80 °C and heated till 180 °C at a rate of 10 °C min \(^{-1}\), followed by further heating till 240 °C at a rate of 4 °C min \(^{-1}\). This temperature was maintained for 2 min. The total area of FAs that flowed into the capillary column was used to determine the relative percentage of each FA.

For phytosterol and tocopherol analysis, the samples were derivatized with \(\text{N,O-bis(trimethylsilyl) trifluoroacetamide trimethylchlorosilane (BSTFA/TMCS)}\) for 30 min at 60 °C. The Sa-cholestanol standard was added (80 \(\mu L\)) to the derivatized samples at a concentration of 5 mg mL \(^{-1}\). Next, the samples were diluted with heptane, thereby obtaining a solution with a concentration of 40 mg mL \(^{-1}\). Identification and quantification of the phytosterols and tocopherols were carried out by adopting a broad-based methodology (Du and Ahn, 2002) using an SH-Rtx-5MS™ capillary column (Shimadzu, 30 m \(\times\) 0.25 mm \(\times\) 0.25 \(\mu m\)). Santos et al. (2015) reported the heating ramp of the column used during the analysis, which was also used by Trentini et al. (2017), Cuco et al., 2019a,b and Stevanato and da Silva (2019) for analysis of other vegetable oils.

### 2.2.6. Antioxidant activity

Analysis of antioxidant activity was performed using the DPPH (1,1-diphenyl-2-picrylhydrazine) (Boroski et al., 2015; Gyamfi et al., 1999) and inhibition of ABTS\(^{+}\) radical (2,2-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid)) (Boroski et al., 2015) free radical scavenging methods using duplicates of each sample, totaling four repetitions of each oil/extract.

#### 2.2.6.1. DPPH method

Ethanol was used to dilute the samples of SFO, SFO + OLE, and OLE to an initial concentration of 2000 μg mL \(^{-1}\). Samples (250, 500, 750, 1000, 1500, and 2000 μL of the solution) were transferred to test tubes containing 2.0 mL of DPPH methanolic solution. After keeping them for 30 min in the dark, absorbance at 517 nm was measured by spectrophotometer (Hach/DR 2800). The reference used was methanol. DPPH antioxidant activity was calculated by Equation (8):

\[
A_{\text{DPPH}}(\%) = \left( \frac{A_{\text{DPPH}} - (A - A_{\text{b}})}{A_{\text{DPPH}}} \right) \times 100
\]

where \(A_{\text{DPPH}}\) is the absorbance of the DPPH solution; and \(A\) and \(A_{\text{b}}\) are the absorbance of the samples and blank, respectively.

The sample concentration capable of reducing 50% of DPPH (EC\(_{50}\)) was calculated from the linear equation, via percentage antioxidant activity versus sample concentration (μg mL \(^{-1}\)).

#### 2.2.6.2. ABTS\(^{+}\) method

The reference antioxidant used for the calibration curve was the Trolox standard (6-hydroxy-2,5,7,8-tetramethylchroman-2-carboxylic acid). The ABTS\(^{+}\) reagent was dissolved in water at a concentration of 0.007 mol L \(^{-1}\) and then reacted with a solution of potassium persulfate (0.140 mol L \(^{-1}\)), forming the ABTS radical. The solution was diluted in ethanol and calibrated on a spectrophotometer (Hach/DR 2800) until the absorbance reached 0.70 ± 0.05 at a wavelength of 734 nm.

Samples (30 mL) of SFO and OLE at concentrations of 250, 1200, and 2000 mg mL \(^{-1}\) were prepared and pipetted in test tubes. Then, 3 mL of ABTS\(^{+}\) solution was added to the test tubes and homogenized. After 6 min in the dark, absorbance at 734 nm was measured on a spectrophotometer (Hach/DR 2800). The results were calculated from the Trolox calibration curve equation and expressed in mmol of Trolox per g of oil or extract.

### 2.2.7. Oxidative stability

The oxidative stability of the oils was determined using the Rancimat method (Metrohm). The reaction vessel containing 3.0 g of oil was connected to the heating block of the equipment, where the sample was exposed to the airflow of 20 L h \(^{-1}\) at a constant temperature of 120 °C (Damanik and Markovic, 2018; Farhooch and Hoseini-Yazdi, 2014). Secondary oxidation products were loaded into the measuring vessel containing 50 mL of ultrapure water and recorded in the order of increasing conductivity. The induction time (IT) was determined automatically from the second derivative of the conductivity curve using StabNet Software (version 1.1) (Metrohm, 2019).

### 2.2.8. Statistical analysis

The Tukey test was used to test the contrasts between the treatment means (extraction methods and plant matrices) and to verify whether there was a difference between the treatments (SFO, SFO + OLE, and OLE) concerning oxidative stability, antioxidant activity, FAs, and IT, using SISVAR software version 5.7 (Ferreira, 2014).

Mass percentage yield results were submitted to t-student test at 5% significance using Statistica software, version 8.0 for each group of samples in each analysis. Values followed by different letters indicate significant differences.

The multivariate method of principal component analysis (PCA) was used to reduce the number of variables and to evaluate the contribution of the FAs and active compounds in the SFO, SFO + OLE, and OLE, using the computational package FactoMineR (R Studio Inc., Boston, MA, USA) (Luo et al., 2009).

### 2.2.9. Process modelling and simulation

In view of the possibility of scaling up this extraction process, its requirements were modeled and simulated with the process simulator.
Aspen Plus® V12.0 for the purpose of evaluating assessing its technical and economic feasibility. The chemical components present in the characterization analysis were considered and the process simulation was designed at the same experimental conditions. According to the simulator methods assistant, NRTL-RK was selected as the equilibrium calculation data and property method, with the Redlich-Kwong equation of state for fugacity coefficient (vapor phase) and the NRTL model for activity coefficient (liquid phase), based on the type of interactions existing in the system’s compounds and operating conditions. The plant location for the scaled-up designed process is based on the availability of sunflower grains and olive leaves, being selected São Paulo in the southeast region of Brazil, and the process flowsheet is presented in Fig. 1. At the beginning of the process, a spare tank (TANK) is used to mix the make-up propane with process recycling in order to maintain the process solvent regeneration, which is posteriorly pressurized (PUMP) and heated and (HE1) for achieving the required process conditions. Heat losses of 5% were assumed for heat exchangers and isentropic efficiency of 80% was considered for pumping. Next, the solvent stream (SOLVPROP) is fed into the solid-liquid extractor (EXTRACT), which operates with a heating jacket to keep the isothermal process. At the exit of the extractor, the extract stream containing the products (PRODUCT) goes to a backpressure valve (BACK-PV) to return the pressure at the set point value. In sequence, the products and solvent are separated using a flash tank separator (SEP) operating at room temperature and 1 bar, where propane is recovered in the recycle stream (PROP-R) while the liquid phase containing all oils is removed at the bottom. The scaled-up scenario was designed for processing 2.4 tonnes of a mix containing sunflower grains and olive leaves, being selected S. arabvinen, 2020) were considered to annualize the capital expenditure in the economic analysis (i.e., the capital investment is applied on a plant life span along 10 years under an interest rate of 10%). Then, both expenditures are summed and the total annualized cost (TAC) is obtained according to Eq. (12).

\[
EACC \left[ \frac{US\$}{yr} \right] = \frac{i (1 + i)^n}{(1 + i)^n - 1} \quad (11)
\]

\[
TAC \left[ \frac{US\$}{yr} \right] = EACC \left[ \frac{US\$}{yr} \right] + OPEX \left[ \frac{US\$}{yr} \right] \quad (12)
\]

where \( n \) represents the time horizon of the designed process (years) and \( i \) is the effective rate of return adopted for the investment.

For calculating part of operating costs, Table 1 presents the prices adopted based on the Aspen Process Utility costs databank and market references aligned to a similar work developed in the Brazilian scenario (Barros et al., 2022).

Table 1

| Stream/Utility | Cost unit | Value | Reference |
|----------------|-----------|-------|-----------|
| Propylene | US$/kg | 20 | Messer Gases (2021) |
| Cooling Water | US$/kg | 0.0004 | Aspen Process Utility |
| Low pressure Steam | US$/kg | 0.0179 | Aspen Process Utility |
| Electricity | US$/kW | 0.0775 | Aspen Process Utility |

and management. Complementarily, fixed costs of insurance, local charges and plant overhead, general administrative, distribution, research and development are also are also covered by OPEX (Eq. (10)) (Turton et al., 2018).

\[
CAPEX \left[ \frac{US\$}{yr} \right] = C_{\text{direct}} \left[ \frac{US\$}{yr} \right] + C_{\text{indirect}} \left[ \frac{US\$}{yr} \right] \quad (9)
\]

\[
OPEX \left[ \frac{US\$}{yr} \right] = C_{\text{maintenance}} \left[ \frac{US\$}{yr} \right] + C_{\text{charges}} \left[ \frac{US\$}{yr} \right] + C_{\text{general}} \left[ \frac{US\$}{yr} \right] \quad (10)
\]
expenses, the supervision and direct administrative costs, and operating labor costs. Additionally, the general expenses are considered at around 15% of the sum of the EACC and remaining manufacturing costs (i.e., the total production cost). A straight-line depreciation was assumed considering 10% per year over the period of operation, which indicates a low residual value of the equipment at the end of the project’s useful life.

Essentially, the formulated oil is priced higher than conventional seeds oils already produced on a large scale due to its health benefits and incorporation of bioactive compounds. The average price of the seeds oil in its fresh form is considered as US $66.83 per liter, which is obtained from online stores (Amazon, 2021; Americanas, 2021; Ebay, 2021; Sulu, 2021). It is necessary to highlight that instead of comparison purposes with other extraction techniques, the focus of this work is to investigate the possibility of establishing a pressurized propane extraction plant to get high-quality SFO + OLE close to the market requisites. Finally, the economic indicators selected to evaluate the economic performance of the designed scenario are the Net Present Value (NPV), calculated based on the difference between the annual gross profits obtained selling the product along and the equivalent annual costs (EACC) a whole year, and the payback period, representing the time to recuperate the capital investment (Turton et al., 2018).

3. Results and discussion

3.1. Mass percentage yield

Table 2 shows the mass percentage yields of the extractions using the different plant matrices (SFO, SFO + OLE, and OLE) and the two extraction methods, (SOX and PRO).

All the average yields of the matrices extracted alone (sunflower grains and olive leaves) or together (sunflower grains + olive leaves) were higher by the conventional method (SOX) when compared to the pressurized propane (PRO) extraction method: 46.8% higher for SFO, 3.1% for OLE, and 50% for SFO + OLE. Extraction via the Soxhlet method is known to promote the total extraction of lipids and nonpolar components in propane and the shredded leaves within the extraction vessel (that act as physical impediments to the process) are factors that prejudiced the extraction yield. Besides that, the oil content in olive leaves is inherently low (Jaski et al., 2019a,b). Despite the low extraction yield using only olive leaves (1%), the composition’s high quality is covered in the following sections.

The Sovová kinetic model was used to evaluate the kinetic extraction curves. The following characteristics were used for the calculations: initial oil concentration in the inert solid = 0.67 g and bed porosity = 0.75 for sunflower grain samples; and initial oil concentration in the inert solid = 0.22 g and bed porosity = 0.75 for samples of sunflower grains + olive leaves.

Table 3 indicates the results of the adjustable parameters calculated for the Sovová model and the solubility of the oils in the solvent (propane). The dynamic method was used to calculate these parameters from the linear part of the extraction curves.

The model presented a good correlation coefficient for SFO (0.9926) and SFO + OLE (0.9988), meaning that there is a good correlation between the model variables, both for SFO and SFO + OLE.

The addition of olive leaves to the extraction bed provided an increase in the parameter r due to the more significant amount of oil mass available for extraction (oil mass of the grains + oil mass of the leaves).

The solubility values (S) calculated for the extraction with olive leaves are lower than those for the extraction performed with sunflower grains. In other words, the model indicates that the use of olive leaves in the extraction bed decreases the solvent’s potential to solubilize the oil. This evidence corroborates the data from the kinetic oil extraction curves (Fig. 2) and mass percentage yield values (Table 2).

The values of the mass transfer coefficients in the solid phase (ksa) were lower than those of kfa (solvent phase) in the extraction pairs (with and without olive leaves), indicating that the reason for the highest extraction yield was the easily accessible oil. This indicates a certain barrier in the diffusion process and the consequent solubilization of oil that is difficult to access, which has been observed in other studies (Zanqui et al., 2020).

The tFER parameter indicates when the easily accessible oil extraction ends, generating a period of decreasing extraction rate. This value was lower in the sample extracted in a structured bed with olive leaves, corroborating the results that indicated a lower yield for these extractions, possibly justified by the mechanical impediment that the leaves generated in the extraction bed. This parameter also justifies not prolonging the extraction time since the difficult-to-access oil does not usually contribute significantly to the extraction yield (Sovová et al., 1994).

3.2. Fatty acids

Table 4 shows the FA composition in all plant matrices extracted by conventional (SOX) and pressurized (PRO) methods.

The lipid profile of SFO extracted with olive leaves remains the same. All the FAs present in pure SFO appear in the chromatographic profile of SFO + OLE. The primary purpose is to evaluate the acquisition of SFO + OLE. OLE also features FAs in its composition, with emphasis on saturated fatty acids (SFAs) and PUFAs (Ghanem et al., 2019), and the SOX method extracts a more significant amount of linoleic acid (25.7 ± 0.9%) while PRO extracts more oleic acid (24.0 ± 0.2%). SFO stands out for its high content of oleic and linoleic acids for the two extraction methods (PRO and SOX), an advantageous characteristic of the grains of this species, which can vary according to the agronomic characteristics of the species, varying conditions in plant cultivation, growing regions, material collection time, and other factors (Figueiredo et al., 2008; Grulova et al., 2015; Martínez-Force et al., 2015; Nimet et al., 2011; Onemli, 2012).

It is important to know the fatty acid profile of the oils, because n-6 FAs, as well as n-9 are considered essential because the human body does not produce them, and they provide health benefits such as the

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Table 2: Mass percentage yield of sunflower oils (SFO), sunflower oil extracted with olive leaves (SFO + OLE), and olive leaves extract (OLE), obtained by conventional method by Soxhlet equipment (SOX) and pressurized propane (PRO).

| Sample          | Yield (%) | SOX | PRO | CV (%) |
|-----------------|-----------|-----|-----|--------|
| SFO             | 46.8±0.6  | 39.6±0.2 | 1.1  |
| SFO + OLE       | 50.0±0.2  | 32.4±0.4 | 0.8   |
| OLE             | 3.1±0.1   | 0.8±0.3  | 9.8   |

Mean ± Standard deviation; Different letters in the same line indicate significant difference (p < 0.05).
3.3. Active compounds

To analyze the active compounds, the composition of SFO, SFO + OLE, and OLE was evaluated. The purpose of this analysis was to identify the main active compounds present in each of the matrices (isolated or together) and to quantify the increment promoted by the addition of olive leaves in SFO + OLE.

Table 5 presents the results of the quantification of active compounds for oils obtained by different methods.

In general, simultaneous extraction of olive leaves with sunflower grains provided the incorporation of active ingredients. This incorporation is evident when observing the amount of α-tocopherol in SFO and its increase in SFO + OLE, regardless of the extraction method. There was a 53% increase of this active compound using SOX and a 35% increase using SFO. The high content of α-tocopherol (about 66 mg 100 g⁻¹) in SFO is already known, and this addition of tocopherols to the oil further enhances its beneficial properties for use and consumption. In the literature, the data show that α-tocopherol is a potent antioxidant, neutralizing free radicals or reactive oxygen species (ROS) (Aggarwal et al., 2010). Also, α-tocopherol is studied to fight cancer and protect against bone, cardiovascular, eye, and neurological diseases (Aggarwal et al., 2010; Peh et al., 2016).

β-Sitosterol was the main phytosterol from olive leaves incorporated into SFO by both extraction methods. Extraction with pressurized propane promoted its incorporation in SFO + OLE (91%), while for extraction by the conventional method (SOX), 69% was incorporated when compared to SFO. Besides that, the active compounds present exclusively in the leaves of the olive tree (1-octacosanol and 1-triaccontanol), which were not detected without SFO, now appear incorporated in SFO + OLE (Table 5).

The phytosterols observed in the extract and in the oil obtained are compounds of high added value that could be used in foods in the future (Moreau et al., 2018b). The extraction of these compounds with propane and with sunflower oil as co-solvent had not been studied in the literature. The present work showed that the extraction process is directly related to the incorporation of active compounds in sunflower oil.
Table 4
Composition of fatty acids in relative percentage present in sunflower oil (SFO), sunflower oil extracted from olive leaves (SFO + OLE) and olive leaf extract (OLE), obtained by conventional method by Soxhlet equipment (SOX) and pressurized propane (PRO).

| Component (%) | SOX | SFO | SFO + OLE | PRO | SFO | SFO + OLE | OLE |
|---------------|-----|-----|-----------|-----|-----|-----------|-----|
| Lauric acid   | 0.1 ± 0.1 | 0.1 ± 0.1 | 0.3 ± 0.1 | 0.3 ± 0.1 | 0.1 ± 0.1 | 0.6 ± 0.1 |
| (C12:0)       |     |     |           |     |     |           |     |
| Myristic acid | 0.1 ± 0.1 | 0.1 ± 0.1 | 2.2 ± 0.1 | 0.1 ± 0.1 | 0.1 ± 0.1 | 2.3 ± 0.1 |
| (C14:0)       |     |     |           |     |     |           |     |
| Palmitic acid | 6.1 ± 6.5 | 23.6 ± 6.3 | 6.2 ± 4.9 | 6.9 ± 7.2 | 26.4 ± 6.2 | 26.4 ± 6.2 |
| (C16:0)       | 0.1 | 0.1 | 0.6 | 0.1 | 0.1 | 0.1 |
| Stearic acid  | 4.3 ± 4.3 | 4.9 ± 4.9 | 5.1 ± 5.1 | 5.3 ± 5.3 | 6.0 ± 5.3 | 6.0 ± 5.3 |
| (C18:0)       | 0.1 | 0.2 | 0.3 | 0.1 | 0.1 | 0.1 |
| Linolenic acid| 0.1 ± 0.1 | 25.7 ± 0.1 | 0.1 ± 0.5 | 0.1 ± 0.5 | 15.5 ± 0.5 | 15.5 ± 0.5 |
| (C18:3-3)     | 0.1 | 0.1 | ± 0.9 | 0.1 | 0.1 | ± 0.4 |
| Arachidic acid| 0.4 ± 0.4 | 3.9 ± 0.4 | 0.4 ± 0.5 | 0.5 ± 0.5 | 4.5 ± 0.5 | 4.5 ± 0.5 |
| (C20:0)       | 0.1 | 0.1 | 0.2 | 0.1 | 0.1 | 0.2 |
| Palmitoleic acid| 0.1 | 0.1 | 0.4 | 0.1 | 0.1 | 0.6 |
| (C16:1)       | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Oleic acid (C18:1 9) | 48.0 | 47.5 ± 14.2 | 45.6 | 45.3 ± 24.0 | 45.6 ± 24.0 | 45.6 ± 24.0 |
| ± 0.1 | 0.2 | ± 0.2 | ± 0.1 | 0.1 | 0.2 |
| Linoleic acid | 38.3 | 39.0 ± 8.8 | 38.4 | 37.7 ± 10.6 | 37.7 ± 10.6 | 37.7 ± 10.6 |
| (C18:2 6)     | ± 0.1 | 0.7 | 0.6 | ± 0.1 | 0.1 | ± 0.4 |
| Lignoceric acid| 0.4 ± 0.4 | ± 0.5 | 0.5 ± 0.5 | N.D. | N.D. | N.D. |
| (C24:0)       | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| Behenic acid  | 1.2 ± 1.2 | 6.9 ± 1.5 | 1.5 ± 1.6 | 3.2 ± 1.0 | 3.2 ± 1.0 | 3.2 ± 1.0 |
| (C22:0)       | 0.1 | 0.1 | 0.6 | 0.1 | 0.4 | 0.4 |
| SFA           | 12.8 | 13.4 ± 47.1 | 14.8 | 15.4 ± 45.9 | 15.4 ± 45.9 | 15.4 ± 45.9 |
| ± 0.2 | 0.5 | ± 0.1 | ± 0.1 | 0.1 | ± 0.7 |
| MUFA          | 49.1 | 48.6 ± 16.3 | 46.7 | 46.4 ± 26.3 | 46.4 ± 26.3 | 46.4 ± 26.3 |
| ± 0.1 | 0.6 | ± 0.3 | ± 0.2 | 0.1 | ± 0.7 |
| PUFA         | 38.3 | 38.5 ± 34.6 | 38.5 | 38.2 ± 26.1 | 38.2 ± 26.1 | 38.2 ± 26.1 |
| ± 0.1 | 0.7 | ± 0.4 | ± 0.1 | 0.1 | ± 0.2 |

SFA: saturated fatty acids, MUFA: monounsaturated fatty acids, PUFA: polyunsaturated fatty acids. N.D.: not detected.

Ultrasonic extraction of phytosterols from olive leaves (Orozco-Solano et al., 2010) showed that the compounds found in this work (β-sitosterol, campesterol, and octacosanol) were also observed, and the major compound found was also β-sitosterol. Smaller fractions of oil produced from the residue containing bagasse, leaf, bark, and olive seeds contain octacosanol and triacontanol (which was also incorporated into SFO + OLE) (Fernández-Arche et al., 2009), both of which are indicated to inhibit cholesterol (Singh et al., 2006). Other studies have shown their cholesterol-lowering properties, as well as their anti-aggregating effect (Taylor et al., 2003).

The practical contribution of OLE compounds to SFO is evidenced by the PCA in the next section.

Fig. 4 shows Principal component analysis (PCA) relating the first and second principal components (Dm1 and Dm2) to the composition of active compounds (A) with the matrix and methods extraction. The first two dimensions summarize 99.4% of the chemical composition relative to the active compounds of SFO, OLE, and SFO + OLE, extracted by different methods (conventional and pressurized propane). Dm1 separates OLE on the positive axis, regardless of the extraction method, and on the negative axis, it groups OLE and SFO + OLE in the mean antioxidant activity (ABTS) between the extraction matrices as a function of the extraction method. For both propane extraction and the conventional method, SFO + OLE showed a higher antioxidant activity (ABTS) when compared to SFO. Olive leaves have a natural anti-oxidant potential to replace the synthetic antioxidants commonly used in vegetable oils.

Generally, the antioxidant content in SFO and other plant-based oils is not high. Sunflower seeds have an IC50 of around 1022 µg (Zilli et al., 2010), values similar to those found in this study (Table 6). Pumpkin seed oil has an IC50 of ~926 µg and when extracted together with the pumpkin peel results in an IC50 of ~750 µg (Curo et al., 2019a,b), with a lower IC50 value indicating an increase in antioxidant potential, similar to the increase found in the present study with the use of propane as solvent (Table 6). Therefore, a significant increase in the antioxidant content in vegetable oils, even by small amounts, is of great interest for improving the quality of the oil, especially without the use of synthetic compounds.

Synthetic antioxidants are often used in commercial vegetable oils to increase their durability, favoring their commercialization for a longer time. The relative effectiveness of antioxidants depends on their solubility in oil, and lipophilic antioxidants more effectively protect oils against oxidation (Abdalla and Rooney, 1999; Frankel et al., 1982). Therefore, the joint extraction of vegetable matrices (sunflower grains and olive leaves) can favor the acquisition of soluble antioxidants in the same extraction solvents as vegetable oils (propane or hexane). This discovery explains the significant increase in the protection of the incorporated oil (SFO + OLE) with the compounds of the olive leaves.

Table 6 shows the comparison between the IT in oils extracted from sunflower grains (SFO) and from seeds + leaves (SFO + OLE). SFO extracted with propane showed an IT of approximately 1.8 h, similar to that found in previous experiments by other researchers (Nimet et al., 2011), and the conventionally extracted oil had an IT of 1.2 h. The statistical analysis showed no difference in the mean IT for the two oils (p < 0.05).
according to the extraction method. Regarding matrices, SFO + OLE was more resistant to oxidation than pure SFO.

SFO + OLE showed an increase in IT of about 2.7 and 3.7 h compared to SFO for the PRO and SOX methods, respectively. There was an increase in IT of at least 150%. This increase is more significant than the 2.5 h reported by Farahmandfar et al. (2018), who used natural antioxidants from lemon essential oil in SFO after oil extraction. The increase in IT is similar to that found for the synthetic antioxidant TBHQ.

Table 5
Quantification of the active compounds (in mg.100g−1) present in sunflower oil (SFO), sunflower oil extracted from olive leaves (SFO + OLE), and olive leaf extract (OLE), obtained by conventional method by Soxhlet equipment (SOX) and pressurized propane (PRO).

| Sample | Active compounds (mg per 100 g oil) | SOX | PRO | SOX | PRO | SOX | PRO | SOX | PRO | SOX | PRO | SOX | PRO |
|--------|-------------------------------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
|        | α-Tocopherol                        |     |     |     |     |     |     |     |     |     |     |     |     |
| SFO    | 65.9 ± 0.3                          | 66.3 ± 3.8 | ND | ND | 16.8 ± 1.1 | 12.7 ± 0.4 | 15.5 ± 0.9 | 15.4 ± 0.7 | ND | ND | 81.9 ± 1.9 | 66.4 ± 2.5 |
| SPO + OLE | 109.0 ± 2.6                      | 89.8 ± 8.4 | 11.5 ± 1.1 | 15.7 ± 0.1 | 12.8 ± 1.3 | 12.4 ± 0.5 | 16.1 ± 0.9 | 16.3 ± 0.7 | ND | 8.5 ± 0.3 | 138.5 ± 0.6 | 127.0 ± 0.6 |
| OLE    | 894.0 ± 0.3                         | 631.4 ± 8.4 | 286.8 ± 1.0 | 287.0 ± 0.1 | ND | ND | 36.0 ± 0.9 | 53.6 ± 3.7 | 97.6 ± 3.7 | 147.3 ± 5.3 | 1158.6 ± 3.7 | 960.5 ± 3.7 |

ND: not detected.
This technology may be feasible for replacing the synthetic antioxidants commonly added to SFO, taking advantage of a residue from olive growing.

These data demonstrate the high potential of using this process to obtain oils with better oxidative stability without synthetic antioxidants after extraction. The addition of OLE to the extraction process provided the oils with a longer IT than in other studies. The increased resistance of vegetable oils to degradation is essential for the food industry. Increasing the shelf life of vegetable oils without synthetic antioxidants is what industries need to add value to the final product and not harm consumers’ health.

3.5. Scaled-up process performance and economic perspectives

Table 7 and 8 presents the mass and energy balances, respectively, of the process simulation performed in Aspen Plus, indicating compositions and operating conditions of the main streams of the process, and the energy flows of equipment. From the perspective of energy consumption of the process, it is notable that heat exchangers for adequacy of solvent temperature and flashing the products for separation are the main responsible operations for thermal energy requirements, while pressurizing the solvent covers almost the total electricity requirement. Moreover, because of the process demand in each process unit, the equipment data sizing obtained by APEA supplement for the industrial
scenario are listed in Table 9 following the nomenclature of Fig. 1, added by unit costs. The extractor plays a key role in the process and equipment highlights, with a volume of 515 L designed with an internal height and diameter of 4.88 and 0.46 m, respectively, which is a feasible proportion.

Based on the size of equipment previously described, the capital expenditures were predicted for acquisition and installing the industrial-scale plant, and are showed in upper section of Table 10 also considering indirect expenses demanded to build it. In view of a representative and complete economic estimation, the charges and property insurance taxes evaluated are around at 4% and 1%, respectively, referencing total CAPEX (Table 10).

Following the economic assessment with all costs, an industry with the potential of processing 792 tonnes per year of grains/leaves reaches a processing cost estimated at around 6.93 US$ per kg of raw material. Consequently, in terms of investment distribution, costs converted directly from the mass balances indicate that the final oil may be obtained at a cost of 31.5 US$ per tonne of oil. Overall, the associated costs in terms of their annual fractions represent 4.1% and 95.9% for the CAPEX and OPEX, respectively, and, depending on the applications and the commercialization market purity requirements, profitable scenarios are expected.

Under the economic assessment, Fig. 5 presents a cumulative cash flow diagram if the planning/construction period of the industrial plant is executed in 2 years. Along this period, the required initial investments before starting up the industry are the capital expenses to build the plant and the floating capital to start its operation (both values indicated in Table 10). The final NPV is calculated as positive (1.05 \times 10^7 US$ after 10 years) and the required period to recuperate the initial investment (payback) is 6.2 years, i.e., 8.42 years if the construction period is considered. Consequently, even under different design and operating conditions the NPV and payback period values are in accordance with the results found in similar works (Kayathi et al., 2020, 2021). Overall, the studied extractive process may be considered economically feasible since the operating conditions and process performance are maintained.
4. Conclusion

The use of olive leaves simultaneously with sunflower grains in a structured bed for extraction with pressurized propane and for conventional Soxhlet extraction with hexane proved effective for incorporating active compounds, with emphasis on 1-octacosanol and β-sitosterol. There was a 53% increase in traditional Soxhlet extraction with hexane proved effective for incorporating olive leaf extract by the conventional extraction technique and a 35% increase in pressurized propane extraction. Also, there was a significant of increase greater than 3 hours in the IT for oils obtained from olive leaves, which implies a product with more significant antioxidant potential. The economic evaluation elucidated the economic potential of establishing a unit for simultaneous extraction of sunflower seeds and olive leaves with pressurized propane. The process is considered economically feasible with a positive NPV and a payback period of 6.2 years. Thus, this study concludes that it is possible to use an innovative and cleaner process without toxic solvents and a conventional process for the aggregation of chemically active compounds in sunflower oil by the combined use of vegetable matrices. This process has advantages due to the small amounts of solvent required, short extraction time, elimination of post-processing steps, and a high potential for promoting the products’ healthiness.

CRediT authorship contribution statement

Jonas Marcelo Jaski: Writing – original draft, Writing – review & editing, Investigation, Conceptualization, Formal analysis, Data curation. Karen Keli Barbosa Abrantes: Writing – original draft, Formal analysis, Data curation. Ana Beatriz Zanqui: Writing – original draft, Writing – review & editing, Conceptualization. Natalia Stevanato: Formal analysis, Data curation, Writing – original draft. Camila da Silva: Formal analysis, Data curation, Supervision. Carlos Eduardo Barão: Supervision, Conceptualization, Investigation. Lucas Bonfim-Rocha: Writing – original draft, Formal analysis, Data curation. Lúcio Cardozo-Filho: Supervision, Conceptualization, Investigation, Writing – review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors thank São Paulo Research Foundation (FAPESP) (Grants No. 2017/03614-0), and, the Improvement of Higher Education Personnel (CAPES) (Process No 88887.354426/2019-00).

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