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Alternative oil extraction methods from *Echium plantagineum* L. seeds using advanced techniques and green solvents

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A B S T R A C T

The edible oil processing industry involves large losses of organic solvent into the atmosphere and long extraction times. In this work, fast and environmentally friendly alternatives for the production of echium oil using green solvents are proposed. Advanced extraction techniques such as Pressurized Liquid Extraction (PLE), Microwave Assisted Extraction (MAE) and Ultrasound Assisted Extraction (UAE) were evaluated to efficiently extract omega-3 rich oil from *Echium plantagineum* seeds. Extractions were performed with ethyl acetate, ethanol, water and ethanol:water to develop a hexane-free processing method. Optimal PLE conditions with ethanol at 150 °C during 10 min produced a very similar oil yield (31.2%) to Soxhlet using hexane for 8 h (31.3%). UAE optimized method with ethanol at mild conditions (55 °C) produced a high oil yield (29.1%). Consequently, advanced extraction techniques showed good lipid yields and furthermore, the produced echium oil had the same omega-3 fatty acid composition than traditionally extracted oil.

1. Introduction

The vegetable oil extraction industry uses large volumes of hexane and long extraction times which cause environmental problems due to direct losses of organic solvents into the atmosphere; hence, greener alternatives are needed. In recent years, there have been important advances in the development, optimization and applications of green extraction techniques in the food industry to reduce the environmental impact by waste minimization, to decrease energy consumption and processing time and to avoid health hazards by substituting toxic and unsafe solvents (Kerton & Marriott, 2013). The combination of advanced extraction techniques with green solvents provides shorter extraction times, less solvent use and decreases energy consumption, making an overall extraction process more environmentally friendly (Chemat et al., 2017). Recently, the solvent selection guide CHEM21 (Prat et al., 2016), based on a benchmark of existing guides, classified the most common solvents in four categories: recommended or preferred, problematic, hazardous and highly hazardous. The ranking has been developed in order to promote the use of recommended solvents, such as ethanol and water, and to avoid the hazardous and highly hazardous solvents. In spite of hexane is a solvent allowed for food industry by the Food and Drug Administration (FDA) and the European Commission, it is classified as hazardous and as non-preferred solvent by international authorities (European Parliament, Council of the European Union, 2008, Office of the, 2011). Therefore, identifying ways to reduce solvent use and replacement of hexane during process development with an environmentally friendly solvent is becoming a priority for the food industry (Chemat, Fabiano-Tixier, Vian, Allaf, & Vorobiev, 2015; Jessop, 2016; Tobiszewski, Tsakovski, Simeonov, Namiesnik, & Pena-Pereira, 2015).

Alternative extraction solvents, like ethanol, water and even ethyl acetate, are greener processing fluids for oil separation from oilseeds against the present methods with hexane and they should be tested first in new developed methods to establish if there is any incompatibility in process conditions (Prat et al., 2016). Thus, more environmentally friendly options are in request and a number of methods using green solvents have been studied with a wide range of bioactive compounds (Plaza & Turner, 2015) and different oil sources such as sunflower seeds (Ravber, Knez, & Škerget, 2015) or soybeans (Phan, Brown, White, Hodgson, & Jessop, 2009).

Echium plantagineum L. is an herbaceous plant belonging to the Boraginaceae family which produces numerous small seeds with high oil contain, around 30% (Gray, Payne, McClements, Decker, & Lad, 2010). The oil is characterized by a high percentage of omega-3 polyunsaturated fatty acids, such as alpha-linolenic and stearidonic acid. In the last few years, echium oil has been considered a possible renewable source of omega-3 as an alternative to oil derived from fish; furthermore, it is available on the market as a novel food ingredient with the authorization of the FDA (Food and Drug Administration, 2004) and the European Commission (European Parliament and of the Council, 2008).

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The industrial production of echium oil involves extraction of crushed seeds using food grade hexane and isolation of the oil removing solvent by vacuum distillation. However, there are no references to report oil production from *Echium plantagineum* by new extraction techniques and green solvents.

Advanced extraction techniques such as pressurized liquid extraction (PLE), microwave assisted extraction (MAE) and ultrasound assisted extraction (UAE) allow the use of green solvents in fast methods providing new sustainable strategies and tools to replace the traditional extraction processes. The most commonly applied methods for recovery of oil and fat from different sources are old traditional methods which include Soxhlet, Folch or Bligh and Dyer, and involve the use of elevated volumes of organic solvents and time-consuming procedures. In contrast, the advantages that offer modern extraction techniques are shorter extraction times, greener solvents, less solvent use, full automation and greater reliability (Señoráns & Luna, 2012).

PLE is an alternative for extraction that combines high temperature and pressure with liquid solvents to achieve rapid and efficient extracts from multiple matrices (Castejón, Luna, & Señoráns, 2017; Conte et al., 2016). When the solvent used is pure water, PLE technique is called subcritical water extraction. In the same way, MAE can work under pressure at closed vessels, though the extraction of analytes implies the use of microwave energy. Microwave heating is very selective and the effect is strongly dependent on the dielectric constant of the matrix, chemical compounds and solvent nature. In recent years, MAE has been used for extraction from different plant materials, including seeds (Delfan-Hosseini, Nayebzadeh, Mirmoghtadaie, Kavosi, & Hosseini, 2017). In contrast, UAE implies the use of ultrasound waves generated by a water bath or an ultrasonic probe which produce cell disruption and facilitates the extraction by the cavitation phenomenon. Ultrasound technology is applied for green and economically viable extraction of food and natural extracts (Chemat et al., 2017, Tiwari, 2015). Consequently, three advanced extraction techniques were selected to evaluate the oil production efficiency with clean solvents from a novel source of omega-3 fatty acids, echium seeds.

Therefore, the main objective of this study was to evaluate the use of modern extraction techniques and green solvents to extract omega-3 fatty acid rich oil from echium seeds and compare with traditional method with hexane. Extraction conditions using PLE, UAE and MAE with ethyl acetate, ethanol, water and their mixtures as solvents, were optimized to achieve fine hexane-free alternatives. Furthermore, fatty acid compositions of extracted oils were analyzed in order to assess the content of omega-3 fatty acids at different conditions, techniques and solvents used and to evaluate the extraction performance.

2. Materials and methods

2.1. Materials

Echium seeds (*Echium plantagineum* L.) were provided by Technology Crops International (Essex, United Kingdom). Seeds were ground with a particle size less than 500 µm using a grinder (Moulinex-A320R1 700 W) and stored at 4 °C until their use. Ethyl acetate, hexane and methanol were purchased from Lab Scan Analytical Sciences (Gliwice, Poland). All solvents were HPLC grade. Absolute ethanol (PRS grade), sodium hydrogen carbonate and potassium hydroxide were purchased from Panreac Quimica S.A (Barcelona, Spain). The water used was Milli-Q grade (Millipore, USA). Fatty acid methyl esters standard (Supelco 37 FAME Mix) was from Supelco (Bellefonte, PA, USA).

2.2. Oil extraction methods

Oil extractions from ground echium seeds were carried out using different techniques: Soxhlet, PLE, MAE and UAE. The experiments were done in all cases at least in duplicate.

2.2.1. Soxhlet extraction

Ground echium seeds (5.00 g) were extracted with hexane in a Soxhlet apparatus by a continuous series of cycles of boiling and condensation of solvent for 8 h.

2.2.2. Pressurized liquid extraction

PLE was carried out with an extractor ASE 350 DIONEX (Sunnyvale, California) equipped with stainless steel extraction cells (10 mL volume). Ground echium seeds were weighed (3.00 g) and loaded into the extraction cell. Then, the extraction cell was filled with the different solvents used: ethyl acetate, hexane, ethanol, water and mixtures of ethanol:water in different proportions (90:10, 80:20, 70:30 and 50:50 V/V) and heated at 60, 90, 120 and 150 °C for the first three solvents and 120, 150 and 200 °C for ethanol:water and water. Static extraction time was 10 min for each experiment and the used solvent volume was 20–25 mL, depending on the temperature and pressure of the cell. Finally, the extract was recovered under a nitrogen stream in vials of 50 mL.

2.2.3. Microwave assisted extraction

MAE were carried out with a MLS 1200 Mega Microwave Lab Station (Milestone Srl, Sorisole, Italy) and a conventional microwave CMI (Les Ulis, France) with maximum power up to 900 W. Ground echium seeds were weighed (3.00 g) and added in Teflon vessels with 30 mL of solvent (solid/solvent ratio = 1/10 (w/V)). Extractions were performed with two methods: open vessel for ethyl acetate and hexane and closed vessel for polar solvents (ethanol, ethanol:water (50:50) and water). Experiments were carried out at different extraction times and using a microwave power range between 270–540 W and, for the specific case of hexane, 900w. Depending on the extraction time, solvent and microwave power, the temperature reached different values. Temperature in closed vessel system was measured by a temperature sensor which was inserted in the vessels and, for open vessel system temperature was measured with a temperature probe at the end of the extraction time.

2.2.4. Ultrasound assisted extraction

UAE was carried out with an ultrasound bath Elmasonic S 40H Elma brand (Singen, Germany) with automatic control of time and temperature and ultrasound frequency of 37 kHz. Ground echium seeds were weighed (3.00 g) the and different solvents tested such as ethyl acetate, ethanol and hexane were added (solid/solvent ratio = 1/10 (w/V)) in vials of 50 mL. Different experiments were carried out at 30, 55 and 80 °C for 15 and 30 min of extraction time. Finally, the extract was filtered using a cellulose filter and collected.

The samples were evaporated in a rotary evaporator (Heidolph Hei-Vap Value HB/G3, Germany) under reduced pressure at 40 °C and dried under a nitrogen stream until constant weight. The oil content was determined gravimetrically and expressed as dry weight percentage. Oils obtained by each extraction technique were stored in dark vessels with nitrogen atmosphere at 4 °C until their analysis.

2.3. Analysis of fatty acid composition by GC-MS

Previous to analysis on an Agilent GC–MS series 5975 MSD (Palo Alto, Cal., USA), fatty acid methyl esters (FAMEs) were freshly prepared by base-catalyzed methanolysis of the glycerides (KOH in methanol). FAMEs were separated using a HP 88 capillary column (100 m × 0.25 mm, i.d. 0.2 µm) (Agilent, CA, USA). 1 µL sample was injected using a split ratio of 1:100. The column was held at 175 °C for 10 min after injection, the temperature-programmed at 3 °C/min to 220 °C and held for 20 min more. Helium was used as carrier gas, at a constant column flow rate of 1.5 mL/min. The injector temperature was 250 °C and the detector temperature was 230 °C. The mass spectrometer was operated at 70 eV with a mass range from 30 to 400 amu. FAMEs were identified comparing their retention times and the mass spectra