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Optimization of high pressure extraction processes for the separation of raspberry pomace into lipophilic and hydrophilic fractions

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A B S T R A C T

Berry juice production residues are used inefficiently and in many cases are wasted, due to a lack of valorization of their processing methods. This study provides an example of biorefining of raspberry pomace by using high pressure extraction. Lipophilic fractions were isolated by pressurized liquid extraction (PLE) with hexane or supercritical carbon dioxide extraction (SFE-CO_2), while the residues were re-extracted with polar solvents, methanol or ethanol. Optimal parameters were established by Central Composite Design and Response Surface Methodology. The yields of lipophilic and hydrophilic fractions were up to 15 and 25%, respectively. Antioxidant properties of extracts were evaluated by total phenolic content (TPC), trolox equivalent antioxidant capacity (TEAC) and oxygen radical absorbance capacity (ORAC). Polar fractions were remarkably stronger antioxidants, e.g. TPC of hexane and methanol extracts were 5.37–10.15 and 26.31–38.95 mg/g gallic acid equivalents, respectively. Raspberry pomace extracts may be promising ingredients for functional foods, nutraceuticals, cosmetics and other applications.

1. Introduction

Berries are rich sources of dietary antioxidants and other bioactive compounds. Many berry species also possess excellent sensory properties and are consumed fresh; however, fresh fruits are highly perishable; therefore large fractions of their harvests are processed into longer shelf life products such as juice, jams, and others. Pressing of berry juice results in high amounts of residues, which are called press-cake, pomace or marc. If such residues are not processed into other products they are considered a waste. Generally, Directive 2008/98/EC [1] defines waste as '*any substance or object which the holder discards or intends or is required to discard*' whereas 'bio-waste' means biodegradable waste. In addition, the same Directive indicates that '*a substance or object, resulting from a production process, the primary aim of which is not the production of that item, may be regarded as not being waste but as a by-product only if the specified conditions are met*'. In scientific literature other terms, such as 'production residues', 'crop residues' (generated in the farm) and 'agro-industrial residues (generated during post-harvest process) have also been used.

According to the FAO [2], roughly one-third of the edible parts of food produced for human consumption is lost or wasted globally. This amount accounts about 1.3 billion t/year and reflects not only the food processing wastes, but also the "food losses" [3]. Currently the majority of wastes are used inefficiently, while they may be converted into high added value food grade ingredients [4]. Fruits and vegetables are among the most important agricultural products resulting in immense amounts of residues; for instance, in juice processing press-cakes the dry solids discharge constitutes approximately 30%. Currently large amounts of juice production residues containing valuable bioactive constituents such as polyphenolic antioxidants, vitamins, pectin, lipids, and other substances are discarded as a waste or used for composting, while numerous articles report the possibilities of recovery of such substances by using both conventional and novel technologies.

Regardless of an increasing number of studies on recovery of valuable components from fruit waste, industrial production and commercialization of such products remain insufficient. Moreover, research has been focussed mainly on the waste of the major horticultural products such as citrus fruits [5], grapes [6,7], olives [8], pomegranates [9] and apples [10], while numerous other vegetable, fruit and berry species remain underexplored. Therefore, the concept of biorefining should be wider applied for the development of high added value functional ingredients from food grade waste and by-products [11]. Particularly promising trend may be considered development of complex processing and separation methods, which include conventional and novel techniques for the recovery of high added value constituents. For instance, supercritical fluid,

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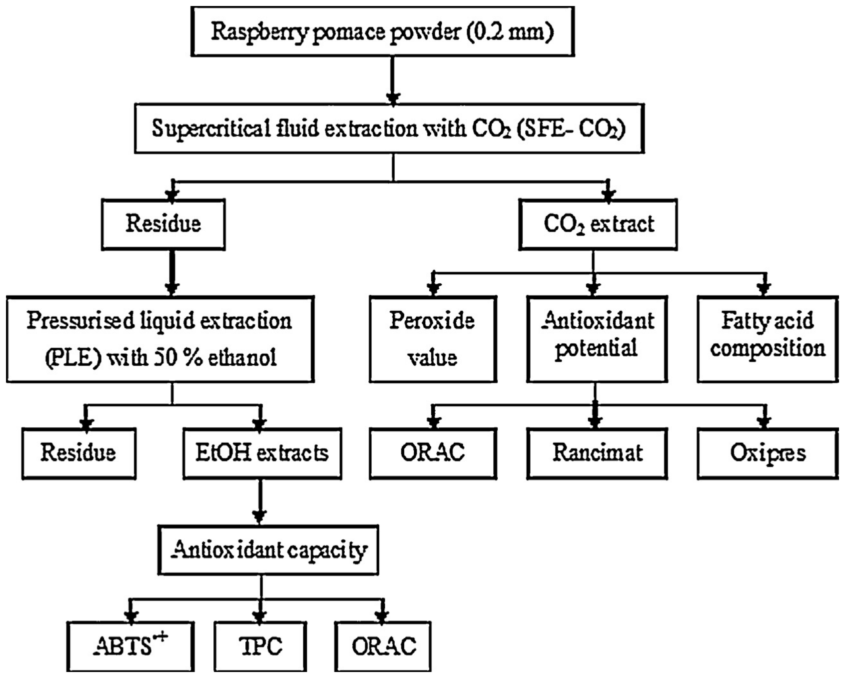

Fig. 1. Biorefining scheme of raspberry pomace by supercritical fluid (SFE-CO_2) and pressurized liquid (PLE) extraction.

pressurized liquid, microwave and ultrasonic assisted extraction and fractionation, chromatographic separation and purification, microbial, enzymatic, chemical and thermal treatment methods as well as their combinations are promising opportunities for the conversion of agricultural residues into valuable materials, which may find numerous applications, e.g. in the development of functional foods, nutraceuticals, natural food additives, cosmetics, pharmaceuticals, etc. Innovative application and optimization of these processes may result in achieving an ideal' 'zero-waste' objective.

Raspberries are important berries in many countries; their annual production is constantly growing and currently exceeds 0.5 million tons per year. The main producers are Russia, Poland, USA, Serbia and The Ukraine. Previously raspberry pomace was reported to possess stronger antioxidant and antimicrobial properties and to contain higher concentrations of total phenolics and ellagitannins than the whole fruit and pulp [12]. Raspberry pomace extracts isolated with 80% methanol demonstrated favorable non-tumor/tumor cell growth ratios and potently increased the apoptosis/necrosis ratio in breast adenocarcinoma and cervix carcinoma cells [13]. However, all previously performed studies used conventional extraction techniques and only one study [14] reported extraction of raspberry pomace by using supercritical carbon dioxide; the authors obtained 5.2% of raspberry pomace extract, however they did not optimize the process and did not apply further biorefining schemes.

The aim of this study was to develop an innovative 2-step high pressure fractionation process of raspberry pomace by optimizing the parameters of supercritical fluid extraction with carbon dioxide (SFE-CO_2) and pressurized liquid extraction (PLE) for the isolation of the highest yields of lipophilic and hydrophilic fractions and to assess antioxidant properties of the obtained fractions. In addition, development and application of green technologies for the production of natural ingredients have become more attractive in terms of safety and environmental protection. Extraction with carbon dioxide and ethanol may be partially considered as green technologies.

2. Materials and methods

2.1. Plant material, chemicals, solvents

Fresh raspberry (*Rubus idaeus* L.) pomace was obtained from the local juice producer in Kaunas region (Lithuania). They were kept frozen at −20 °C before freeze-drying. $K_2S_2O_8$ was from Lach-Ner (Brno, Czech Republic), Na_2CO_3, fluorescein, 2,2′-azobis(2-amidinopropane)dihydrochloride (AAPH) gallic acid, 2,2′-azinobis(3-ethylbenzothiazoline-6-sulfonic acid)diamonium salt (ABTS), β-cyclodextrin from Sigma–Aldrich (Steinheim, Germany), Folin–Ciocalteu's reagent from Sigma–Aldrich (Buchs, Switzerland), methanol (99.8%) from Lachema (Brno, Czech Republic), food grade ethanol from Stumbras (Kaunas, Lithuania), carbon dioxide (99.9%) from AGA (Vilnius, Lithuania).

2.2. Extract preparation

Freeze-dried raspberry pomace was ground in an ultra-centrifugal rotor mill Retsch ZM200 (Retsch, Haan, Germany) using 0.2 mm particle size sieve. Two series of raspberry pomace fractionation experiments were carried out: (1) consecutive extraction with hexane and methanol under pressurized conditions and (2) consecutive extraction with supercritical carbon dioxide (SFE-CO_2) and pressurized ethanol (Fig. 1). In the first series, PLE with hexane and methanol was performed in 10 mL extraction cells of an accelerated solvent extraction apparatus ASE 350 (Dionex, Sunnyvale, CA, USA). Dried material was mixed with diatomaceous earth and placed in the cell with two cellulose filters at the top and in the bottom. Extraction pressure was constant (10.3 MPa), while temperature and time were in the range of 30–110 °C and 5–25 min, respectively based on CCD experiment modeling (Table 1).

SFE-CO_2 experiments were carried out in a supercritical fluid extractor Helix (Applied Separation, Allentown, PA, USA). Each extraction was performed from 10 g of ground raspberry pomace placed in a 50 mL cylindrical extractor (14 mm × 320 mm; $h/d = 22.86$) between two layers of defatted cotton wool in both