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Effects of the extraction conditions on the yield and composition of rice bran oil extracted with ethanol—A response surface approach

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ABSTRACT

Rice bran oil was obtained from rice bran by solvent extraction using ethanol. The influence of process variables, solvent hydration (0–24% of water, on mass basis), temperature (60–90 °C), solvent-to-rice bran mass ratio (2.5:1 to 4.5:1) and stirrer speed (100–250 rpm) were analysed using the response surface methodology.

The extraction yield was highly affected by the solvent water content, and it varied from 8.56 to 20.05 g of oil/100 g of fresh rice bran (or 42.7–99.9% of the total oil available) depending on the experimental conditions. It was observed that oryzanol and tocols behave in different ways during the extraction process. A larger amount of tocols is extracted from the solid matrix in relation to γ-oryzanol. It was possible to obtain values from 123 to 271 mg of tocols/kg of fresh rice bran and 1527 to 4164 mg of oryzanol/kg of fresh rice bran, indicating that it is feasible to obtain enriched oil when this renewable solvent is used. No differences in the chemical composition of the extracted oils were observed when compared to the data cited in the literature.

Keywords: Solubility; γ-Oryzanol; Tocopherols and tocotrienols; Fatty acid composition

1. Introduction

Crude rice bran oil (RBO) stands out among the other edible oils because a unique antioxidant and nutraceutical complex is present in its composition. The unsaponifiable fraction (up to 5% mass of crude oil) contains approximately 0.9–2.9% of γ-oryzanol and 100–1000 mg kg^{-1} of tocopherols and tocotrienols, hereafter referred to as tocols. These minor compounds have been cited in the scientific literature as powerful antioxidant agents that are effective in preventing degenerative diseases (Orthoefer, 1996; MacCaskill and Zhang, 1999; Lerma-García et al., 2009).

Tocols have proven effective in preventing cardiovascular disease and some forms of cancer, whereas oryzanol, a mixture of triterpene alcohols and phytosterols esterified with ferulic acid, has shown hypocholesterolemic activity and is effective in decreasing early atherosclerosis and inflammatory processes (Xu, 2008; Zigoneanu et al., 2008; Imsanguan et al., 2008).

Rice bran, a low-value co-product obtained from rice processing, could represent a potential source of healthy products due to the nutritional aspects mentioned above. The rice bran yield is approximately 8–10% paddy rice, and its oil content varies between 14 and 18% depending on its geographical origin, seed varieties and extracting methods. This means a 10–12 kg yield of crude oil/ton of processed rice, which may represent a significant additional income for rice producers (Orthoefer, 2005; Monsoor and Proctor, 2005; Zullaikah et al., 2009).

Rice bran oil (RBO) is popular in several countries, such as Japan, India, Korea, China and Indonesia, where this product is extensively consumed as an edible oil. However, despite the positive nutritional characteristics and the possibility of economical benefits for the rice industry, rice bran oil production

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is below its potential, especially in Brazil. This fact is mainly due to the geographic decentralisation of the production and mills and the difficulties in the oil extraction and refining process. According to Ghosh (2007), RBO is difficult to process due to its high levels of free fatty acids (FFAs), waxes, bran fines and pigment content. These factors lead to high refining losses when traditional refining processes are employed. However, with careful attention to processing techniques, beginning with the rice mill, one can produce RBO economically with reasonable yields and quality (Ghosh, 2007).

In fact, the rice bran oil extraction method used, either mechanical or solvent extraction, and the solvent used, are also decisive determinants of the crude rice bran oil quality obtained and, thus, the final content of minor compounds, γ-oryzanol and tocols (Rodrigues and Oliveira, 2010).

In general, RBO is extracted from rice bran using hexane as a solvent. Although this solvent presents high stability and high capability for dissolving oil as its main advantages, it is considered a neurotoxin and is toxic at high concentrations (Hammond et al., 2005). In addition, it is related to environmental pollution, besides its fossil origin.

In recent years, the oil industry has shown increased interest in alternative solvents because of environmental and safety concerns. Several types of solvents have been proposed to replace hexane as the extractant of vegetable oils: trichlorethylene, water with or without enzymes, halogenated hydrocarbons, aldehydes (furfural), ketones, D-limonene, short-chain alcohols, and supercritical carbon dioxide, among others (Johnson and Lusas, 1983; Rosenthal et al., 1996; Liu and Mamidipally, 2005; Kuk and Hron, 1998; Proctor and Bowen, 1996; Hu et al., 1996; Xu and Godber, 2000; Franco et al., 2007, 2009; Monsoor and Proctor, 2005; Imsanguan et al., 2008; Zigoneanu et al., 2008; Amarasinghe et al., 2009).

Ethanol has gained attention as a potential solvent for vegetable oils and has been studied for oil extraction from soybeans (Arnold and Choudhury, 1962; Rodrigues et al., 2010), corn (Moreau and Hicks, 2005), and cottonseed (Sineiro et al., 1998; Abraham et al., 1988). In general, previous studies of solid–liquid extractions carried out with ethanol showed a higher extraction of sugars, phosphatides, pigments and waxes and yielded a better meal compared to that obtained with hexane (Beckel et al., 1948; Regitano-d'Arce et al., 1994).

In this work, the feasibility of using ethanol as an alternative extraction solvent for rice bran oil was investigated from the perspective of the quality of the extracted oil. In other words, the influence of some process parameters was studied: temperature, solvent water content, stirrer speed and solid-to-solvent mass ratio as well as their effect on the extraction yield and extractability of minor compounds, γ-oryzanol and tocols. The data were analysed using the response surface methodology (RSM), and in general, non-linear multiple regression allowed us to obtain models with a reliable and acceptable predictive capability. The influence of the independent variables on the fatty acid composition of the extracted oil was also evaluated.

2. Materials and methods

2.1. *Materials*

The solvents used in this work were absolute ethanol (Merck, Germany) with purity greater than 99.5% and aqueous solvents with varying moisture contents ranging from 6 to 24%, on a mass basis that were prepared by diluting absolute ethanol with deionised water (Millipore Direct-Q 3-UV, Molheim, France).

Rice bran was stabilised and formulated in pellets in the refinery (Irgovel/NutraCea, Pelotas, Brazil) using a pre-set and patented combination of heat, water, and pressure, without the use of chemical products. The pellets were stored at −20 °C to prevent enzymatic deterioration (Orthoefer, 2005) until they were submitted to the extraction process.

The oil content in the rice bran was determined with a Soxhlet apparatus (Tecnal, Piracicaba, SP, Brazil), using petroleum ether as the solvent according to the Am 2-93 official method (AOCS, 1998). The protein content was determined according to the Ac 4-91 Kjeldahl total nitrogen method (AOCS, 1998). The rice bran moisture content was determined according to the Ac 2-41 official method (AOCS, 1998). All measurements were performed in five replicates.

As previously commented, the main aim of this work was to study the influence of several parameters of the RBO extraction process using ethanol as the solvent. To enable the visualisation of possible effects of the aforementioned variables on the chemical composition of oils obtained by ethanol, the fatty acid composition and content of nutraceutical compounds; the composition of these extracts were compared with the composition of an extract obtained via the methodology suggested by Bligh and Dyer (1959). The use of oil obtained by cold extraction, as suggested by Bligh and Dyer, is justified because, when using this method, the lipids are extracted without heat, ensuring the correct quantification of the levels of free fatty acids, vitamin E, sterols and the correct determination of the fatty acid composition. In fact, the oil extracted via the Bligh and Dyer method was used as a reference, which made it possible to measure the effects of independent variables on the composition of ethanol extracts.

The RBO, extracted from rice bran pellets according to the cold method suggested by Bligh and Dyer (1959), was characterised in terms of free fatty acids by titration (IUPAC, 1979) and the level of gamma-oryzanol was determined by spectrophotometry, using a UV-Vis dual beam spectrophotometer (model UV 1650 PC, Shimadzu, Japan) at 314.5 nm (Seetharamaiah and Prabhakar, 1986). The tocol quantification (tocopherols and tocotrienols) was determined at 520 nm according to the methodology developed by Emmerie-Engel (Parrish, 1980). This characterisation procedure was accomplished before each extraction trial.

The RBO extracted according to Bligh and Dyer's methodology was also analysed by gas chromatography of the fatty acid methyl esters to determine the fatty acid composition according to the Ce 1-62(97) official method (AOCS, 1998). Prior to the chromatographic analysis, the fatty samples were prepared in the form of fatty acid methyl esters according to the Ce 2-66(97) official method (AOCS, 1998). A Shimadzu 2010 AF capillary gas chromatograph (Japan) with an automatic injector (Shimadzu, model AOC 20i, Japan) and a flame ionisation detector was used under the following experimental conditions: Crossbond-PEG 0.25 μm, 30 m × 0.25 mm id. (RTx-Wax, Restek, Bellefonte, PA, USA) capillary column; helium carrier gas at a rate of 0.74 mL/min; injection temperature of 250 °C; column temperature of 160–245 °C (rate of 3 °C/min); detection temperature of 280 °C; and injection volume of 1.0 μL. The fatty acid methyl esters were identified by comparison with external standards purchased from Supelco (Bellefonte, PA, USA). The quantification was accomplished by internal normalisation.