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Ethanol extraction of rice bran oil, a value added activity for rice bran valorization in a Madagascan context

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A B S T R A C T

Rice is the staple food of the Madagascan people and rice bran is valorized as animal feeding. The possibility to use deoiled rice bran in animal feed has been demonstrated by some researchers, and it appears to have no negative impact on animal growth performance. The aim of this work is to investigate whether it would be worth introducing the rice bran oil (RBO) extraction in the chain of exploitation of rice by-products to bring value added activity. Ethanol produced locally from plant waste was used as a solvent. It has been demonstrated that oil contains a good quality of antioxidant with 24-methylene cycloartanylferulate as the main Oryzanol compound and β and γ-tocotrienols as the main tocols. After comparing oil qualities, it was shown that ultrasonication is the most appropriate technique yielding 9.40% oil within an extraction time of 50 min whilesoxhlet extraction onlygave 7.05% oil within 360 min of extraction duration. Oleic acid and linoleic acid are the main fatty acid compounds. Stabilization is an important step before the extraction because the physico-chemical properties of the RBO have shown signs of alteration due to the absence of this preliminary treatment. Nevertheless, RBO extraction is beneficial and its implementation in the rice by-products exploitation cycle could contribute to the development of the rural economy of Madagascar.

Keywords: Rice bran oil, ultrasound extraction, green solvent, Oryzanol, tocols, reverse HPLC.

1. Introduction

Rice is the staple food for Madagascan people.According to the Food and Agriculture Organization, 2021 rice paddy production in 2020 was 4.23 million tons. This would yield between 0.22 and 0.34 million tons of rice bran. Rice bran is largely used for animal feeding in the country. Wal,1972has described rice bran, as being "*not truly a by-product of rice milling*", for it is a co-product that is valorized in animal feeding. Since then however, the situation has not much evolved. The aim of this work is to evaluate the possibility to insertrice bran oil (RBO) extraction in the chain of valorization as a value added activity. The idea is not to substitute the use of rice bran in animal feeding, but rather to add a supplementary economically valued activity, the defatted rice bran, being anyway used for animal feed. Some researchers have demonstrated that defatted rice bran can be included in pig diets as a substitution for corns and soybean meal (Huang, 2021).It can also be implemented in poultry meal (Bhanja, 2001, Adrizal, 1996).

Oryzanol, tocols and sterols are among the important compounds that make of the RBO, a great source of functional food (Punia, 2021). Oryzanol and tocols contents of the extracted RBO are studied in this work. Fatty acids and sterol contents of RBO from some Madagascan rice varieties have already been investigated. It has been concluded that there is no significant variation in the quality of RBO from different varieties (Gaydou, 1980). Thus only one variety was chosen to be studied in this work, the *Makalioka*, which is estimated to be the best rice quality in the local market (Sakurai, 2015). Hexane is still the most commonly used solvent for RBO extraction despite its toxicity and its polluting effect (Garba, 2017).Ethanol is a co-product of agroindustry in Madagascar, but its production quantity could be increased through valorization of biomass waste (Qin, 2021). Ethanol has been chosen for this work as a green solvent. Ultrasound extraction is also considered as a green method. Physico-chemical characteristics and fatty acid compositions of oils obtained from conventional and ultrasound extraction methods were compared. The interest of the use of ultrasound technology is discussed.

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2. Materials and methods

2.1. Rice bran collection

Dried rice paddy was collected from local peasants and authenticated by local specialists as *Makalioka* variety. After milling, the bran was collected and stored away from humidity.

2.2. Soxhlet extraction

Ethanol was purchased from local producers. 500 g of rice bran were extracted with 2 L of ethanolduring 6 hours using soxhlet. The solvent was evaporated in vacuo at 40 to 50°C.

2.3. Identification and quantitation of antioxidant contents

Simultaneous analysis of tocols and oryzanol contents was performed by High Pressure Liquid Chromatography by applying the method developed by Rogers *et a*l., 1993 with some modifications.

2.3.1. Extraction of the antioxidant compounds

500 mg of crude RBO were mixed with 2ml of hexane in a test tube and shaken for 15 s. The sample was then centrifuged at 4 000 rpm. The supernatant was collected for reverse phase HPLC analysis.

2.3.2. Equipment and parameters

LC-6A SHIMADZU chromatograph equipped with a UV detector was used for the analysis. Component separation was performed using C18 column 250 mm * 4.5 mm. Mobile phase consisted of methanol/acetonitrile/dichloromethane/acetic acid (50:44:3:3, by volume). 50µl was injected and the detector was set to scan between 290 nm and 330 nm.

2.4. Comparison of RBO quality obtained by conventional and ultrasound extraction using ethanol as a solvent

2.4.1. Ultrasound assisted extract preparation

Ultrasound bath of 200W with a frequency of 50 Hz was used. The extraction was conducted during 60 min at a temperature of 50°C. The ratio rice bran/ solvent were 1:5 by weight. Sample was then filtrated and the solvent (ethanol) was evaporated in vacuo at 40°C to 45°C.

2.4.2. Physico-chemical quality evaluation

Iodine value was measured using the Hübl method in the presence of mercuric chloride. The other physico-chemical parameters weredetermined according to the Manual of Methods of Analysis of food as described in Oils and Fats, 2012. Quickly, the measurement of acid numberwas carried out by titration with 0.1M of potassium hydroxide using phenolphthalein solution as an indicator. Saponification number was calculated as the amount of potassium hydroxide needed to saponify 1g of RBO. Peroxide value was determined by titrating the iodine released from a solution of sodium thiosulfate. Specific gravity was measured using a pycnometer at 20°C rather than 30°C. The determination of unsaponifiable matter was carried out using diethyl ether as a solvent.

2.4.3. Fatty acid analysis

Determination of fatty acid content was performed by Gas Chromatography analysis of methyl esters. GC-14A SHIMADZU apparatus equipped with Flame Ionization Detector was used. The column was a SOLGEL-WAX of 30m*0.53 mm internal diameter with a film thickness of 1µm. 0.5µl of sample was injected and oven temperature was set at 260°C. The carrier gas was nitrogen with a flow rate of 3 ml/min.

2.4.4. Statistical analysis

Data Comparison of the oil quality from the two extraction methods was carried out using the Bland-Altman method as cited by Grdisa, 2020.

3. Results and discussion

3.1. Extraction yield

Extraction yielded 7.05%. This value is low if compared to literature data. According to Capellini, 2017, the presence of water negatively impacts the extraction performance of the ethanol and it would be possible to reach 16% yield with absolute ethanol. The specific gravity at 20°C was 0.902.

3.2. Tocols and oryzanol contents

Table 1 shows the result of reverse HPLC analysis of these antioxidant compounds.

Table 1 –HPLC analysis of tocols and oryzanol.

Compounds	Retention time (*s*)	Area (*%*)
δ-tocotrienol	253	0.50
β and γ-tocotrienols	313	2.64
α-tocotrienol	363	0.96
α-tocophérol	775	0.40
Cycloartenylferulate	915	13.18
24-methylene cycloartanylferulate	1011	36.36
Campesterylferulate	1259	9.16
Sitosterylferulate	1483	2.33

In descending order, the relative composition of oryzanolis 24-methylene cycloartanylferulate>cycloartenylferulate>campesterylferulate>Sitosterylferulate. This is consistent with literature data, as described by Rogers, 1993. Some varieties of pigmented rice contain a higher number of oryzanolcompounds (Kim, 2013).Among the tocols, β and γ-tocotrienols are the dominant compounds, β and γ-tocopherols are absent.

3.3. Comparison of RBO quality obtained by conventional and ultrasound extraction using ethanol as a solvent

Ultrasound assisted extraction yielded 9.40 % of oil, which is higher than for the soxhlet extraction. As studied by Krishnan, 2015, yield could reach 10.80% with optimum conditions. Compared to the oil obtained by soxhlet extraction method, the specific gravity at 20°C which is 0.909 presented no significant difference.Physico-chemical properties of the oils and the fatty acid compositions are shown in table 2 and table 3 respectively.

Table 2–Comparison of the physico-chemical properties of RBO extracted by ultrasound and RBO extracted by soxhlet using ethanol as a solvent.

Parameters	Ultrasound	Soxhlet
Unsaponifiable matter (%)	4.4	4.1
Acid value (mg KOH/g)	87	92
Iodine value (g/100g)	82	78
Saponification Value (mg KOH/g)	185	195
Peroxide Value (meqO_2/kg)	31.3	36.5

Table 3–Comparison of the fatty acid contents of RBO extracted by ultrasound and RBO extracted by soxhlet using ethanol as a solvent.

Fatty acids	Ultrasound	Soxhlet
Myristic acid	0.47	0.41
Palmitic acid	19.84	17.80
Stearic acid	1.56	1.81
Arachidic acid	0.48	0.72
Palmitoleic acid	0.36	0.30
Oleic acid	38.58	40.25
Gadoleic acid	0.69	0.48
Linoleic acid	36.33	36.62
Linolenic acid	1.71	1.62

Both oils have a very high content of free fatty acid, and the peroxide values are also high. No stabilization was made prior to oil extraction and these values are signs of deterioration. However, ultrasound processing is less destructive than soxhlet extraction. The lower iodine value for soxhlet extracted RBO demonstrates a degradation effect which may be attributed to the temperature. Both oils are suitable for industrial use due to their high saponification values: 185-195 mg KOH/g oil (El-Refai, 2017; Oluremi, 2013). These saponification values are similar to the values for corn oil (187-196 mg KOH/g oil), peanuts oil (184-196 mg KOH/g oil) and olive oil (187-196 mg KOH/g oil) (Bart, 2010). For both oils, oleic and linoleic acid are the major compounds. This is consistent with the results obtained by Oliveira, 2012, also using ethanol as solvent.Figure 1 shows the statistical analysis of the characteristics of the soxhletextracted RBO and the ultrasound extracted RBO. Not all the values are included in the limits of acceptance. The two methods cannot be used interchangeably, meaning that the oil qualities obtained from the two methods of extraction are statistically different.

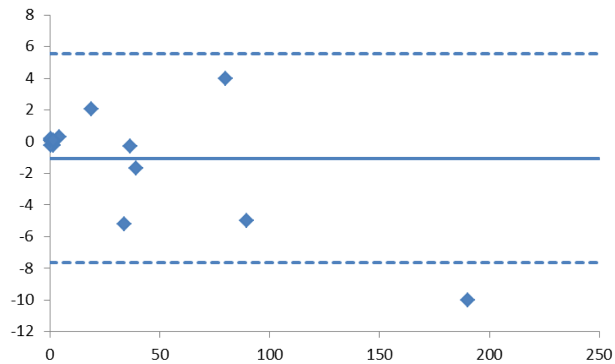

Fig. 1 –Bland Altman analysis of the two methods of extraction.

3.4. Discussion

Ultrasound technology allows the use of alternative green solvents while producing a high quality of oil with a high yield if extraction conditions are optimized (Mushtaq, 2020).This technique also allows the benefit of a short extraction time. In our case, ultrasound extraction lasted only 50 min giving a yield of 9.40% whereas soxhlet extraction lasted 360 min to yield only 7.05%, with the same solvent quality. It can then be inferred that ultrasound extraction technique considerably reduces energy consumption. This advantage is generalized for all seed oil extractions, not only for RBO extraction (Thilakarathna, 2022).As rice is seasonal, ultrasound extraction equipment could be valorized with other activities like extraction of oil from papaya seeds or the extraction of different secondary and primary plant metabolites (Aihua, 2019). Subsequently, it can be argued that RBO extraction with locally produced ethanol solvent can be inserted in the chain ofvalorization of rice by products as a value added activity and the proposed exploitation scheme is shown in figure 2. The rice straw, together with other plant residues can be used for the ethanol production (Malik, 2019; Soam, 2016 and Momayez, 2017). Ethanol can be used as solvent, as well as biofuel which can be used to produce energy for the extraction and the milling units. The biosolvent can also be recycled after extraction to serve as a fuel for the grinding unit.

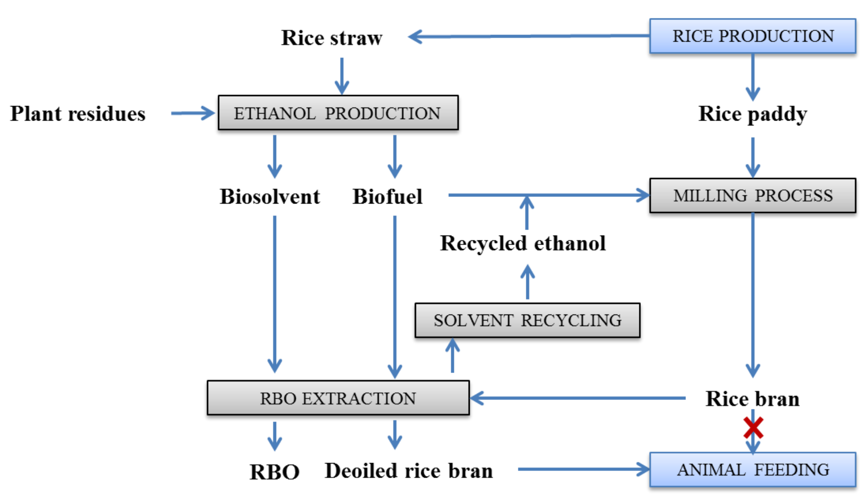

Fig. 2–Proposed exploitation scheme for the insertion of RBO extraction as a value added activity in the rice by products valorization.

4. Conclusion

The present work demonstrated the benefits of performing RBOextraction prior to the use of the deoiled rice bran for animal feeding. Ethanolproduced locally from plant residues can be used as biofuel andbiosolvent. It is possible to obtain a good extraction yield with this solvent using ultrasonication technique, but its extraction performance is reduced if soxhlet is used.The oil has a good quality with acceptable antioxidant content and a good fatty acid profile which is consistent with the literature data. Introduction of this activity in a Madagascan context can contribute to the development of the agricultural economy of the country.

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