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Effect of process variables on the yield and quality of jerivá (*Syagrus romanzoffiana*) kernel oil from aqueous extraction

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SUMMARY: The fruit from jerivá (*Syagrus romanzoffiana*) has a kernel which is rich in oil, and has a pleasant smell that reminds one of coconut. It is rich in monounsaturated and saturated fatty acids, in addition to bioactive compounds. In this work, the effect of process variables on the yield and quality of jerivá kernel oil from aqueous extraction was evaluated using response surface methodology. The variables pH, time and temperature influenced the yield and the quality of the oil. High pH and time, along with mild temperature were suitable conditions to extract jerivá kernel oil by aqueous extraction, but excessively high pH, temperature and time negatively impacted the oil's quality. pH was the only variable that significantly influenced free acidity, with a decrease in free acidity with the increase in pH. On the other hand, the increase in pH, time and temperature increased the peroxide value, which limited some conditions for obtaining jerivá kernel oil by aqueous extraction. The optimal conditions were found to be an extraction at pH 12, 25 °C and 60 minutes, which resulted in a yield of 39%, free acidity of 0.2% and a peroxide value of 5.8 meqO₂·kg⁻¹. Aqueous extraction yielded more unsaturated oil than that extracted with hexane, in addition to a higher proportion of caproic, oleic and linoleic acids, thus improving its nutritional characteristics and health benefits, despite decreasing its oxidative stability.

KEYWORDS: Fatty acid; Lipid; Palm; Response surface methodology

RESUMEN: Efecto de las variables del proceso sobre el rendimiento y la calidad del aceite de almendra de yerivá (Syagrus romanzoffiana) mediante extracción acuosa. La fruta de yerivá (Syagrus romanzoffiana) tiene un grano rico en aceite, que tiene un olor agradable que recuerda al coco, es rico en ácidos grasos monoinsaturados y saturados, además de compuestos bioactivos. En este trabajo, se evaluó el efecto de las variables del proceso sobre el rendimiento y la calidad del aceite de grano de verivá a partir de la extracción acuosa utilizando la metodología de superficie de respuesta. Las variables pH, tiempo y temperatura influveron en el rendimiento y la calidad del aceite. pH alto, elevado tiempo y temperatura suave fueron las condiciones adecuadas para extraer el aceite de grano de yerivá mediante extracción acuosa. Sin embargo, el pH, la temperatura y el tiempo excesivamente altos impactaron negativamente en la calidad del aceite. El pH fue la única variable que influyó significativamente en la acidez libre, con una disminución de la acidez con el aumento del pH. Por otra parte, el aumento del pH, el tiempo y la temperatura aumentaron el valor del peróxido, lo que limitó algunas condiciones para obtener aceite de grano de yerivá por extracción acuosa. Se encontró que la condición óptima fue una extracción a pH 12, 25 °C y 60 minutos, lo que resultó en un rendimiento del 39%, una acidez libre del 0,2% y un valor de peróxido de 5,8 meq O_2 ·kg⁻¹. La extracción acuosa produjo más aceite insaturado que el extraído con hexano, además de una mayor proporción de caproico, oleico y linoleico, mejorando sus características nutricionales y beneficios para la salud, a pesar de disminuir su estabilidad oxidativa.

PALABRAS CLAVE: Ácido graso; Lípidos Palma; Metodología de superficie de respuesta

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1. INTRODUCTION

In recent years, the global consumption of vegetable oil has experienced constant growth. At the same time, the increased demand for vegetable oils as an alternative to petroleum has intensified the competition among potential exporters, contributed to the reduction in inventory levels and low availability of vegetable oils, and also sustained high prices (Coimbra and Jorge 2011; Barbosa *et al.*, 2008). Given the increased demand for oil with different characteristics and applications, the search for new oil sources has become necessary.

The Syagrus romanzoffiana palm, known as queen palm, coco palm or jerivá, is found in most tropical and subtropical areas. The jerivá fruit is a yellowish or orange drupe, with a round or oval shape, with a rigid endocarp covering an oily almond. The almond (kernel) oil has a pleasant smell similar to coconut, is rich in saturated and monounsaturated fatty acids, mainly oleic and lauric, in addition to bioactive compounds, such as phenolics, carotenoids, and tocopherols (Pierezana et al., 2015; Coimbra and Jorge, 2012; Coimbra and Jorge, 2011). jerivá kernel oil (JKO) has interesting characteristics for human consumption (Coimbra and Jorge, 2011; Lescano et al., 2018), but also has potential for biofuel production (Moreira et al., 2013; Falasca et al., 2012).

The conventional methods for oil extraction are organic solvent extraction and screw press. However, another method based on aqueous extraction provides the recovery of oils with good quality and yield. This process comprises milling and stirring the feedstock with water at a suitable pH and temperature, which breaks the vegetable cells and allows the extraction of oil from plant tissues (Khoei and Chekin, 2016; Mat Yusoff *et al.*, 2016). This method has been used efficiently to extract oils from different sources, such as soybeans (Campbell *et al.*, 2011), rice bran (Khoei and Chekin, 2016) and maize germ (Nikiforidis and Kiosseoglo, 2009).

Some process variables can influence the yield and the oil quality in an aqueous extraction, such as feedstock/water ratio, pH, time, temperature and agitation speed, which can vary among different feedstock (Ghorbanzadeh and Rezaei, 2017, Hanmoungjai *et al.*, 2000). Hanmoungjai *et al.*, (2000) reported that agitation speed and solid/water ratio did not influence the yield of rice bran oil in an aqueous extraction process, but about 80% of oil recovery at pH 12 was achieved against less than 40% at pH 3, besides some improvement at high temperature and time. Rosenthal *et al.*, (1998) also observed a higher yield from the aqueous extraction of soybean oil at pH above 8 but verified an irrelevant effect of the solid/water ratio.

An aqueous extraction method can be much safer and more environmentally friendly and economical, mainly compared to solvent extraction. Besides, aqueous extraction can produce oils with characteristics which are different from those extracted by other methods, such as a higher content of unsaturated fatty acids (Ghorbanzadeh and Rezaei, 2017) or lower content of free fatty acid and lower colorimparting components (Khoei and Chekin, 2016). Therefore, an aqueous extraction process can yield JKO which is more unsaturated and with better physicochemical quality than that extracted with an organic solvent. These characteristics can have a positive impact on the use of the JKO for consumption when a high content of unsaturated fatty acids, mainly monounsaturated, is nutritionally desirable (Garcés et al., 2017).

This work aimed to evaluate the effect of process variables on the yield and the physicochemical quality of JKO in an aqueous extraction using a five-level tree-variable central composite design and response surface methodology. In addition, the fatty acid composition and the oxidative stability of the oil from aqueous extraction were determined and compared to the oil extracted with hexane.

2. MATERIALS AND METHODS

2.1. Samples

The jerivá fruits were collected between January and May, 2017 in the south-east region of Brazil (Lavras, Minas Gerais state). All the fruits were collected directly from the ground, and they were ripe, firm and had no injuries. Whole fruits were dried at room temperature for 5 days. After drying, the kernel was separated from the core with the aid of a vice. The moisture was determined immediately before each extraction process Effect of process variables on the yield and quality of jerivá (Syagrus romanzoffiana) kernel oil from aqueous extraction • 3

using a moisture determination balance (i-Thermo 163L – BEL Engineering) at 105 °C.

2.2. Aqueous extraction

About 30 g of jerivá kernels and 300.0 mL of distilled water were milled in a blender for 5 minutes. Then the pH was adjusted according to a factorial design (Table 1) using NaOH 1.0 mol·L⁻¹ or HCl 1.0 mol·L⁻¹. The mixture was agitated in a mechanical stirrer at 500 rpm in a water bath at temperature and time according to the factorial design (Table 1). The mixture was centrifuged (relative centrifugal force of 2150 g) for 10 minutes. In order to break up the emulsion, the upper phase was separated and cooled at -10 °C for 12 h. The material was heated at 60 °C and centrifuged for 5 minutes. The oil was separated, weighed and stored in a closed bottle at -10 °C until analysis. The yield was calculated by:

$$Oil yeld(\%) = \frac{extracted oil(g)}{kernel(g) \times \frac{100 - moisture(\%)}{100}} \times 100 \quad (1)$$

2.3. Solvent extraction

The extraction was carried out in a Soxhlet apparatus using hexane as extractor solvent. After solvent evaporation, the oil was weighed and stored in a closed bottle at -10 °C until analysis.

2.4. Oil characterization

Each of the obtained oils was characterized according to the following parameters:

- *Free acidity*, expressed as the percentage of free oleic acid, according to the AOCS method Ca 5a-40 (2004).
- *Peroxide value*, expressed in milliequivalents active oxygen contained in 1 kg of oil, according to AOCS method Cd 8b-90.
- *Iodine value*, expressed as the amount of iodine absorbed by 100 g of sample, calculated using the fatty acid composition according to AOCS method Cd 1c-85.
- *Saponification value*, defined by the amount in milligrams of potassium hydroxide needed to saponify 1 g of oil or fat, calculated using the fatty acid composition by AOCS method Cd 3a-94.

 TABLE 1.
 Yield, free acidity (FA) and peroxide value (PV) of the jerivá kernel oil from aqueous extraction according to a central composite factorial design. Values predicted by the fitted models are in parentheses

Assay	pH (X1)	°C (X2)	minutes (X3)	Yield (%)	FA (%)	PV (meqO ₂ /kg)
1	8 (-1)	34 (-1)	24 (-1)	33.3±0.3(33.1)	4.1±0.2(3.3)	5.5±0.5(3.3)
2	8 (-1)	34 (-1)	51 (+1)	36.7±0.6(34.4)	4.3±0.5(3.3)	5.7±0.4(2.3)
3	8 (-1)	61 (+1)	24 (-1)	30.6±0.4(30.7)	3.1±0.2(3.3)	5.9± 0.4(3.7)
4	8 (-1)	61 (+1)	51 (+1)	29.4±0.5 (29.5)	2.8±0.1(3.3)	8.9±0.5(4.7)
5	11 (+1)	34 (-1)	24 (-1)	35.9±0.6(34.6)	0.2±0.1(0.3)	9.8±0.3(7.9)
6	11 (+1)	34 (-1)	51 (+1)	36.3±0.5(35.8)	0.2±0.1(0.3)	9.7±0.4(6.8)
7	11 (+1)	61 (+1)	24 (-1)	31.5±0.4(32.2)	0.3±0.1(0.3)	11.7±0.2(8.2)
8	11 (+1)	61 (+1)	51 (+1)	31.5±0.7(31.0)	0.4±0.2(0.3)	13.0±0.4(9.3)
9	7 (-1.68)	47.5 (0)	37.5 (0)	28.2±0.7(28.9)	4.6±0.3(4.4)	6.8±0.5(3.4)
10	12 (+1.68)	47.5 (0)	37.5 (0)	31.1±0.4(31.4)	0.1±0.1(-0.8)	14.5±0.3(11.0)
11	9.5 (0)	25 (-1.68)	37.5 (0)	35.3±0.3(37.3)	1.0±0.2(1.8)	3.2±0.2(4.0)
12	9.5 (0)	70 (+1.68)	37.5 (0)	32.0±0.8(31.2)	$1.7 \pm 0.4 (1.8)$	3.8±0.2(6.4)
13	9.5 (0)	47.5 (0)	15 (-1.68)	33.9±0.5(33.2)	0.8±0.2(1.8)	1.2±0.2(5.2)
14	9.5 (0)	47.5 (0)	60 (+1.68)	31.2±0.6(33.2)	2.0±0.2(1.8)	5.8±0.3(5.2)
15	9.5 (0)	47.5 (0)	37.5 (0)	30.6±0.7(30.1)	1.3±0.1(1.8)	7.8±0.5(7.2)
16	9.5 (0)	47.5 (0)	37.5 (0)	30.2±0.5(30.1)	1.9±0.3(1.8)	6.8±0.4(7.2)
17	9.5 (0)	47.5 (0)	37.5 (0)	29.8±0.4(30.1)	1.9±0.2(1.8)	7.6±0.3(7.2)

Mean \pm standard deviation (n=3).

- Oxidative stability, expressed as the induction period in hours determined using 3 g of sample in Rancimat apparatus at 110 °C with an airflow rate of 20 L·h⁻¹ and 60 mL of distilled water in vials containing electrodes, according to AOCS method Cd 12b-92.
- Fatty acid composition. Samples were transesterified into methyl esters using potassium hydroxide in methanol and n-hexane, according to AOCS method Ce 2-66. The methyl esters were analyzed by gas chromatography (GC-2010 - Shimadzu) equipped with a flame ionization detector and an SPTM-2560 capillary column (100 mm \times 0.25 mm \times 0.2 μ m). The standard used was a mixture of 37 methyl esters (Supelco 37 Component FAME Mix). The following operational parameters were used: split injection mode, split ratio 1:100; 1 µL injection volume; 260 °C detector temperature; 260 °C injector temperature; oven temperature program: held at 60 °C for 1 minute, ramped at 4 °C·min⁻¹ to 140 °C, held for 5 min-utes; ramped at 4 °C·min⁻¹ to 240 °C, held for 30 minutes. Peak identification was resolved by comparing the retention times of the fatty acid methyl ester standards with the retention times of the observed peaks. Quantification was done by normalization (%).

2.5 Statistical analysis

The effects of pH (from 7 to 12), temperature (from 25 to 70 °C) and time (from 15 to 60 min.) on the aqueous extraction process of JKO were evaluated by a five-level tree-variable central composite design (Table 1) and response surface methodology (RSM). The effects were evaluated on yield, free acidity, and peroxide value. The measurements were carried out in triplicate. The models for RSM were fitted using codified variables, and only significant ($p \le 0.05$) regression coefficients were considered. Polynomial models of first-order (linear) or second-order (quadratic) were evaluated by ANOVA in order to find the one that provided the best fit for the data. All calculations and graphs were carried out using Chemoface software (Nunes *et al.*, 2012).

3. RESULTS AND DISCUSSION

3.1. Effect of pH, temperature and time on oil yield

Initially, the effect of pH, temperature, time, agitation speed, and solid/water ratio on oil yield was evaluated in a preliminary study. No relevant effect was detected for agitation speed or solid/water ration. Hanmoungjai *et al.*, (2000) also verified no substantial effect of agitation speed or solid/water ratio on the aqueous extraction of rice bran oil, but pH, time and temperature influenced the

yield. As reported by those authors, it also verified that despite the solid/water ratio being irrelevant for yield, a high solid/water ratio resulted in a mixture which was too hard to be appropriately agitated. Therefore, the solid/water ratio was fixed at 1:10 and the agitation speed at 500 rpm. Extractions at pH below 7 resulted in low yield, and therefore the factorial design considered a pH range above 7.

According to assays from the central composite factorial design, the yield varied from 28% to 37% (Table 1), which corresponds to recoveries from 57% to 76% compared to the yield of 49 g·100 g⁻¹ obtained by extraction with hexane.

The pH values, temperature and time from the factorial design were regressed against the respective yield (Table 1) using least square regression. A quadratic model gave the best fit (Equation 2), with significant regression and non-significant lack of fit (Table 2). The linear coefficients for time, as well as the interactions between pH and temperature and pH and time were non-significant (p > 0.05). The regression coefficients (Equation 2) indicated that temperature (X2) had the greatest influence on the yield, with a larger yield at lower temperatures. The pH (X1) had a small influence, and only its linear coefficient was significant, with a larger yield at

TABLE 2. ANOVA from surface response models for pH, temperature and time over the yield, free acidity and peroxide value of the jerivá kernel oil from aqueous extraction

		SS	DF	MS	F	р
Yield	Regression	88.2	5	17.6	10.7	0.00
	Residual	18.2	11	1.7		
	Lack-of-fit	14.2	8	1.8	1.3	0.45
	Pure error	4.0	3	1.3		
	Total	106.4	16			
	\mathbb{R}^2	0.83				
Free	Regression	31.6	1.0	31.6	101.5	0.000
acidity	Residual	4.7	15.0	0.3		
	Lack-of-fit	1.6	3.0	0.5	2.1	0.15
	Pure error	3.0	12.0	0.3		
	Total	36.2	16.0			
	R ²	0.87				
Peroxide	Regression	157.4	6.0	26.2	7.0	0.00
value	Residual	37.2	10.0	3.7		
	Lack-of-fit	36.7	8.0	4.6	16.4	0.06
	Pure error	0.6	2.0	0.3		
	Total	194.6	16.0			
	\mathbb{R}^2	0.81				

higher pH, which can be verified by comparison of assays 1–4 with 5–6 and 9 with 10 (Table 1). Although the linear coefficient for time (X3) was not significant, its interaction with temperature (X2X3) was significant and negative. Therefore, if lower temperatures resulted in larger yield, this should be more effective at longer times. In fact, the larger yields were reached especially under this condition, such as in assays 2 and 6 (Table 1).

$$Y = 30.13 + 0.74X1 - 1,81X2 - 0.63X2X3 + 1.46X22 + 1.07X32 (2)$$

The response surface in Figure 1-A shows how the yield varied against temperature and time, thus confirming the interaction effect between these variables. It is clear that larger yields were reached especially by combinations of low temperature (25–34 °C) and extended time (51–60 min.). This influence also was evidenced when the pH was considered, wherein for any pH, the yield was large at

mild temperatures (25-34 °C) and at large periods of times (51–60 min.). Initially, the driving force for extraction is high because the concentration gradient of oil between the solid surface and the bulk of the solution is high, but after the initial period, the driving force is low, and the oil has to diffuse from the interior of the solid (Khoei and Chekin, 2016). However, this is overcome by the increase in the solubilization of cell wall components with the increase in extraction time. Despite the tendency of the oil viscosity to decrease with the increase in temperature and favor the withdrawal of oil from plant tissues, excessive temperatures can cause the coagulation of proteins and oil can be trapped in these structures (Ghorbanzadeh and Rezaei, 2017). Considering the coefficients of Equation 2, the temperature had a more relevant effect on the yield than time, and the negative effects of a high temperature can be compensated by a more extensive time of extraction, explaining the significant interaction between these variables.



FIGURE 1. Surface responses for pH, temperature and time over the yield (A, pH fixed at 11), free acidity (B, temperature fixed at 34 °C) and peroxide value (C, temperature fixed at 34 °C) of the jerivá kernel oil from aqueous extraction.

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Regardless of temperature and time, the increase in pH contributed to increasing the yield only slightly. This low effect of pH on the yield can be due to the fact that the tested range of pH (from 7 to 12) is in a maximum extractability range. Similar results also were observed in the aqueous extraction of soybean oil, where a modest increase in extractability was reached along the pH range of 8 to 12, with a steep drop below pH 7 (Rosenthal et al.; 1998). In fact, our preliminary tests revealed that the yields at pH below 7 were low (below 15%), which induced the definition of the pH to be considered in the experimental design. It has been reported that the pH has an effect on the extractability in an aqueous extraction process. The protein solubility, which depends on the isoelectric point of the protein in the oil source, is influenced by pH and affects the extraction of oil from the particles. The stability and solubility of the oleosins which surround the oil droplets are also affected by changes in pH, resulting in a difference in the release of oil droplets from the source. The pH also affects the oleosins in the membrane of fatty tissues, changing its stability and, consequently, the accumulation of fat globules. Therefore, the optimal pH for aqueous extraction of oils from different sources can vary due to the different proteins in their structures (Ghorbanzadeh and Rezaei, 2017; Nikiforidis and Kiosseoglou, 2009). Despite most aqueous extraction processes achieving their greatest yields at high pH due to the protein solubility being highest at basic pH (Campbell et al., 2011; Khoei and Chekin, 2016; Rosenthal et al., 1998), for some oil sources the best pH for extraction can be low (Ghorbanzadeh and Rezaei, 2017).

3.2. Effect of pH, temperature and time over oil quality

RSM was used to evaluate the effect of pH, temperature and time on the free acidity and peroxide value of the JKO from the aqueous process.

The free acidity varied from 0.1 to 4.6% with the different experimental conditions of aqueous extraction, while the oil extracted with solvent had a free acidity of 1.4%. Only the pH (X1) had a significant effect (p < 0.05) on free acidity, which was fitted with a linear model (Equation 3) with significant regression and no lack of fit (Table 2):

$$Y = 1,81 - 1,52X1$$
 (3)

The response surface in Figure 1-B shows how pH and time (considering its non-significant linear coefficient) influenced free acidity, which confirms the irrelevance of the time over free acidity compared to the substantial effect of pH. A similar graph (not presented) also confirmed the irrelevance of the temperature over free acidity when compared to the influence of pH. The increase in pH resulted in a proportional decrease in free acidity, which was probably a consequence of the neutralization of free fatty acids on the alkaline medium of extraction. This effect was also observed in other aqueous extraction processes at high pH, such as for rice bran oil, with a free acidity of less than 0.5% in oils obtained from extractions at pH 12 (Khoei and Chekin, 2016; Hanmoungjai *et al.*, 2000).

The peroxide value of the oils from aqueous extraction varied from 1.2 to 14.5 meqO₂/kg, while the oil extracted with solvent had 9.3 meqO₂/kg. The peroxide value was significantly influenced by pH, temperature and time, which was fitted with a quadratic model (Equation 4) with significant regression and no lack of fit (Table 2):

$$Y = 7.21 + 2.28X1 + 0.72X2 + 0.89X3 + 1.81X12 - 0.72X22 - 0.72X32$$
(4)

pH had the most substantial effect on the peroxide value when compared to the effects of time and temperature. The response surface in Figure 1-C shows how the peroxide value varied with pH and extraction time, which evidences a considerable increase in peroxide value with the increase in pH. This high effect of the pH also was observed when pH and temperature were plotted against the peroxide value (not presented). It is known that the lipoxygenase activity can be increased with an increase in pH, such as for soybean, where the lipoxygenase activity increases in the pH range from 7 to 9 (Ali Asbi et al., 1989). However, this enzyme is quickly inactivated at temperatures between 50 and 70 °C (Ludikhuyze et al., 1998), a range in which high peroxide values were observed in the aqueous extraction of JKO, especially at the most prolonged periods of time. So, a plausible explanation for the observed effects is that the presence of hydroxide ions (OH) can accelerate the hydrolysis of triacylglycerols into diacylglycerols, monoacylglycerols, and free fatty acids through saponification, which corroborates the more substantial effect of pH (larger coefficient in Equation 4) in comparison to time and temperature. These species are amphiphilic compounds and can accelerate the rate of lipid oxidation through the formation of association colloids, once the interface between water and oil is a possible location for lipid oxidation (Chaiyasit et al., 2007; Kim et al., 2016).

3.3. Numerical optimization

A numerical optimization combining all ranges of pH, temperature and time was carried out using the fitted models (Equations 2–4). The optimal condition to maximize yield was found to be pH 12, 25 °C and 60 minutes. On the other hand, numerical optimizations aiming to improve the oil

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quality indicated that extraction at pH 12, 25 °C and 15 minutes minimizes the free acidity, while an extraction at pH 8.6, 25 °C and 15 minutes minimizes the peroxide value. However, the predicted yield on these conditions was low. Then, the optimal extraction at pH 12, 25 °C and 60 minutes was carried out, which resulted in a higher yield of 39%, thus validating the optimized condition. This oil had a free acidity of 0.2%, a peroxide value of 5.8 meqO₂/kg, and was analyzed for fatty acid content and oxidative stability.

3.4. Fatty acid composition and oxidative stability

In general, the oils from aqueous extraction and solvent extraction had a predominance of lauric acid (C12:0) and oleic acid (C18:1) (Table 3). Coimbra and Jorge (2011), Pierezana *et al.*, (2015) and Moreira *et al.*, (2013) also reported JKOs with higher contents of lauric and oleic acid, but other authors also reported the predominance of palmitic (C16:0) and linoleic (C18:2) in addition to oleic (Kobelnik *et al.*; 2011). These variations can be due to effects of region of growth, climate, fruit maturation level, harvest season and extraction method.

The oil from aqueous extraction had a higher proportion of unsaturated fatty acids when compared to the oils extracted with hexane (Table 3). The same was observed for the aqueous extraction of pomegranate seed oil (Ghorbanzadeh and Rezaei, 2017) and *Clanis bilineata* oil (Sun *et al.*, 2018). A higher proportion of short-chain saturated fatty acids (C6:0) and a proportion modestly lower of medium-chain saturated fatty acids

 TABLE 3.
 Fatty acid composition and oxidative stability of the jerivá kernel oil from aqueous extraction

Fatty acid	Hexane extraction	Aqueous extraction	
C6:0	0.8±0.1	2.6±0.2	
C8:0	13.1±0.3	8.4±0.2	
C10:0	11.1±0.3	8.2±0.1	
C12:0	44.0±0.5	33.8±0.4	
C14:0	8.4±0.2	8.6±0.3	
C16:0	4.9±0.1	9.9±0.3	
C18:0	1.8 ± 0.1	2.3±0.1	
C18:1n9c	13.2±0.1	20.3±0.3	
C18:2n6c	2.6 ± 0.2	6.0 ± 0.1	
Σsaturated	84.2*	73.7*	
∑unsaturated	15.8*	26.3*	
Iodine value $(gI_2 \cdot 100g^{-1})$	15.9*	27.8*	
Saponification value (mgKOH $\cdot g^{-1}$)	253.3*	238.5*	
Oxidative stability (h)	23.2±1.0	12.3±0.8	

Mean \pm standard deviation (n=2). *Calculated by the fatty acid averages.

(C8:0 and C10:0) were also verified. The proportion of lauric (C12:0) acid in the oil from aqueous extraction was lower than that found in the oil extracted with hexane. On the other hand, the proportions of long-chain saturated fatty acids (C16:0 and C18:0) were higher, as also occurred for oleic and linoleic. A plausible explanation for these differences can be based on the different affinity of fatty acids for the aqueous medium, which is influenced by the chain length and unsaturation level. It was demonstrated that, although low, the solubility of saturated fatty acids in water increases with the decrease in chain length (Khuwijitjaru et al., 2002) and that monounsaturated (C18:1) and polyunsaturated (C18:2) fatty acids are more soluble in hot water than the saturated fatty acid with equal chain length (C18:0) (Khuwijitjaru et al., 2004). Triacylglycerols with short-chain saturated fatty acids or unsaturated fatty acids would therefore benefit the migration from vegetable tissue to the aqueous medium, which explains the higher proportions of caproic (C6:0), oleic (C18:1) e linoleic (C18:2) acids in the oil from aqueous extraction.

The iodine and saponification values were calculated from the fatty acid profile (Table 3). The iodine value was higher in the oil from aqueous extraction, which was expected because of its higher proportion of unsaturated fatty acids. The oil from aqueous extraction had a slightly lower saponification value, indicating that this oil had a higher average molecular weight of fatty acid when compared to the oil extracted with hexane.

The oil from aqueous extraction showed less oxidative stability (12.3 h) than the oil extracted with solvent (23.2 h). Higher antioxidant activity was reported for oils from aqueous extraction when compared with oils from solvent extraction, which could be due to a higher content of tocopherols in oils from aqueous extraction (Ghorbanzadeh and Rezaei, 2017; Jiao et al., 2014). However, no consistent correlation ($R^2 = 0.26$) was found between tocopherol content and oxidative stability index in a study of the aqueous extraction of pumpkin seed oil (Li et al., 2016). The lower oxidative stability of the oil from aqueous extraction in the present study can be a consequence of the higher proportion of unsaturated fatty acids in the oil from aqueous extraction. Other authors reported oxidative stability of 44.5 h for JKO extracted with petroleum ether (Coimbra and Jorge, 2011) and 21.6 h for oil extracted with hexane (Moreira et al., 2013), which proves the effect of solvent on the oxidative stability of oils.

4. CONCLUSIONS

High pH and time, and mild temperature are suitable conditions to extract jerivá kernel oil by aqueous extraction, but excessively high pH, temperature and time can negatively impact the

oil quality, specially the peroxide value. pH was the only variable that significantly influenced the free acidity, with a decrease in free acidity with the increase in pH. On the other hand, the increase in pH, time and temperature increased the peroxide value, which limited some conditions to obtain jerivá kernel oil by aqueous extraction. The optimized condition was found to be an extraction at pH 12, 25 °C and 60 minutes, which resulted in high yield and low free acidity and peroxide value. The aqueous extraction yielded a more unsaturated oil than the one extracted with hexane, in addition to higher proportions of caproic (C6:0), oleic (C18:1) and linoleic (C18:2) acids, thus improving its nutritional characteristics and health benefits, despite decreasing its oxidative stability.

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Grasas Aceites 71 (1), January-March 2020, e339. ISSN-L: 0017-3495 https://doi.org/10.3989/gya.1063182

Effect of process variables on the yield and quality of jerivá (Syagrus romanzoffiana) kernel oil from aqueous extraction • 9

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