QUALITY AND CHEMICAL COMPOSITION OF RESIDUAL CAKES OBTAINED BY PRESSING JOJOBA SEEDS PRODUCED IN LA RIOJA, ARGENTINA

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Abstract

The objectives of the present work were to compare the chemical composition in a residual cakes (RC) obtained by the industrial pressing process of jojoba seeds harvested in the years 2001, 2002 and 2003 in Bañado de Los Pantanos, La Rioja, Argentina and to analyze the effects of a second pressing process on the residual cakes. The analyzed parameters were moisture, ashes, lipids, proteins, nitrogen-free extract, total phenolic compounds, tannins, acid value, peroxide value, and p-anisidine value. RC 2001 and RC 2002 showed higher lipid content (13.42 % and 10.20%, respectively) and lower protein percentage (23.20 % y 24.86 %, respectively), and also showed higher acid value (6.57 and 5.11 mg KOH/g, respectively), peroxide value (4.58 and 3.65 meq O2/kg, respectively) and p-anisidine (0.80 and 0.75, respectively) than RC 2003. Longer storage time with air contact and higher temperature during the extraction process of jojoba seed wax were the factors that affected the quality of RC.

Key words: Jojoba, oil, residual cakes, composition, quality

Resumen

Los objetivos del presente trabajo fueron comparar la composición química de las tortas residuales (RC) obtenidas por procesos de prensado industrial de semillas de jojoba cultivadas en Bañado de Los Pantanos, La Rioja, Argentina y analizar los efectos

sobre la calidad de RC después de una segunda operación de prensado. Se trabajó con RC de semillas de Jojoba cosechadas en 2001, 2002 y 2003. Los parámetros analizados en RC fueron: humedad, cenizas, lípidos, proteínas, extracto libre de nitrógeno, compuestos fenólicos totales, taninos, valor de acidez, valor de peróxido y valor de p-anisidina. En RC 2001 y RC 2002 se encontraron los mayores contenidos lipídicos (13.42 % y 10.20%, respectivamente) y los menores valores proteicos (23.20 % y 24.86 %, respectivamente), también presentaron los mayores valores para los ensayos de acidez (6.57 y 5.11 mg KOH/g, respectivamente), peróxido (4.58 y 3.65 meq O_2/kg, respectivamente) y p-anisidina (0.80 y 0.75, respectivamente). Tanto el prolongado almacenamiento como la exposición al aire libre y a las altas temperaturas en el proceso de extracción de la cera de las semillas de jojoba fueron los principales factores que afectaron la calidad de RC.
Palabras clave: Jojoba, aceite, tortas residuales, composición, calidad

Introduction

Argentina is on top of the list of countries that export jojoba wax (*Simmondsia chinensis*). Jojoba commercial production in Argentina was favored by the good plant adaptation to the semiarid regions in the province of La Rioja and Catamarca. In La Rioja, there are 720 hectares of jojoba plantations. The main purpose for jojoba production is to get the major component of the seed: jojoba wax.

Jojoba wax is extracted by pressing the kernels several times. The residual matter is known as “expellers”. The press expels the seed wax by strong pressure and heating. Besides the wax, a residual cake (RC) called “press-cake” [1] is also obtained by the pressing process. This “press-cake” can also be repressed.

The Jojoba wax has various applications. It has traditionally been used for cosmetic products. Currently, this wax is also being used as a lubricant additive [1, 2, 3] among other uses. The International Jojoba Export Council [1] defined several universal quality standards for jojoba wax. These standards are affected by several factors related to wax extraction process and/or storage conditions. The main degradation reactions are hydrolysis, chemical or enzymatic oxidation, polymerization, and decomposition, among others. As a result of those reactions, a mixture of secondary oxidation product is formed.

There are studies which tend to give added value to the sub-product: jojoba press-cake. Several authors reported information about methods for the elimination of anti nutritional compounds (simmondsin) found in residual cakes and jojoba seeds [4, 5, 6, 7] and for the conversion of these products into raw material for the preparation of pet food.

In Argentina, the industrial residue obtained in the pressing process of jojoba seed generates an annual accumulation of 1300 tons approximately. This residue could convert into raw material for animal feed and, simultaneously, decrease the negative impact on the environment. In La Rioja province, the jojoba residual cakes obtained from the pressing process are discarded and piled in the open air. Such exposition to weather conditions accelerates the deterioration and oxidation reaction of this material. For animal nutrition, there are several natural products that are residues from industrial process as soybean pellets. These kind of materials are very important ingredient for animal feed but it is necessary, for one side, to characterize their proximal composition specially the protein content and for other side, to preserve their quality against deterioration factors. For that reasons, it is remarkable to characterize the composition and quality of the jojoba press-cake before to destiny this material to animal feed. At

present, the chemical composition and quality of the RC produced in Bañado de los Pantanos, La Rioja, Argentina is still unknown.

The objectives of the present work were to compare the chemical composition in residual cakes obtained by industrial pressing process from jojoba seeds harvested in the years 2001, 2002 and 2003 in Bañado de Los Pantanos, La Rioja, Argentina and to analyze the effects of a second pressing process on the residual cake.

Material and Methods

Materials

Residual cakes (RC) and jojoba seeds were collected in Bañado de Los Pantanos which is located at 67°14' west longitude, 28°36' south latitude and at 865 meters above sea level, province of La Rioja, Argentina. This area has dry weather with 70mm average annual rainfall. The average annual temperature is 20°C with peaks of 46°C in January and minimum temperatures of -4°C in July. In this area, there is no frost during 240 days a year. Winds come mainly from southern/southeast areas, blowing at 49.68 to 55.89 miles/h. Agrinsa Agroindustrial S. A. provided the RC (2001, 2002 and 2003) obtained by industrial pressing where the pressing conditions were the followings: the pressure was around 200 tn/cm^2 and the temperature was between 60-75ºC.

The material samples were taken from different lot of production for each year. The samples were the followings:

- Residual cake 2001 (RC 2001): Obtained by industrial pressing of jojoba seeds harvested and pressed in 2001. Each sample corresponded to different day of production during 2001: Sample #1 produced on August 16th, Sample #2 produced on September 11th and Sample #3 produced on October 12th. All samples were stored *in situ* (piled up in the open air exposed to the environmental condition mentioned above) and recollected and analyzed in 2003.

- Residual cake 2002 (RC 2002): Obtained by industrial pressing (double pressing process) of jojoba seeds harvested and pressed in 2002. Each sample corresponded to different day of production during 2002: Sample #1 produced on August 20th, Sample #2 produced on September 13th and Sample #3 produced on October 17th. All samples were stored *in situ* (piled up in the open air exposed to the environmental condition mentioned above) and recollected and analyzed in 2003.

- Residual cake 2003 (RC 2003): Obtained by industrial pressing (double pressing process) of jojoba seeds harvested and pressed in 2003. Each sample corresponded to different day of production during 2003: Sample #1 produced on August 15th, Sample #2 produced on September 16th and Sample #3 produced on October 14th. All samples were stored *in situ* (piled up in the open air exposed to the environmental condition mentioned above) and recollected and analyzed in 2003.

- Laboratory residual cake 2003 (LC 2003): Three samples of LC 2003 were obtained by lab scale hydraulic pressing (at room temperature) of jojoba seeds harvested in 2003. Each sample was taken from different silo. The hydraulic press works on a stainless steel piston-cylinder device made of. The pressure used over the jojoba seeds was around 600 Kg/cm^2.

Chemical analyses

Three Samples (30g) were taken at random from each residual cake. Each sample was milled in a homogenizing grinder until a uniform size material was obtained (0.75mm mesh). The moisture content was determined by the method 27.005 [8]. Kernels were milled and oil was extracted for 16 h with petroleum ether (boiling range 30-60°C) in a Soxhlet apparatus. Lipid percentage was determined by weight difference.

Ash and nitrogen contents were determined according to the AOAC methods 27.009 and 27.007, respectively [8]. Ash was performed by incineration in a muffle furnace at 525°C. The nitrogen content was converted to protein percentage by using the conversion factor 6.25 (method 27.007, [8]). Nitrogen-free extract (NFE) was quantified by difference. The following formula was used: 100 - (% moisture + % ashes + % lipids + % proteins).

Acid value (AV) and peroxide value (PV) analyses were performed according to AOAC [8]. AV and PV were expressed as mg KOH/g and miliequivalents of active oxygen per kilogram of wax ($meqO_2/kg$), respectively. The *p*-anisidine value was evaluated following the IUPAC method [9]. The *p*-anisidine reagent was prepared with 0.25 g *p*-anisidine hydrochloride (BDH Laboratory Reagents, Poole, England) each 100 mL solution in glacial acetic acid. The absorbances of samples were measured at 350 nm in a spectrophotometer (Perkin Elmer Lambda 25 UV/Vis Spectrometer, Bucks, United Kingdom). The *p*-anisidine value was given by the formula: $PAV = 25 \times (1.2As-Ab) \times (m^{-1})$, where "As" is absorbance of the fat solution after reaction with the *p*-anisidine reagent, "Ab" is the absorbance of the fat solution and, "m" is the mass of the jojoba wax in grams.

Total phenolic and tannin compound contents were obtained and analyzed according to the method described by Price and Butler [10]. The Folin-Ciocalteu reagent (Anedra, San Fernando, Buenos Aires, Argentina) was used to determine total phenolic compound content with a spectrophotometer (Perkin Elmer Lambda 25 UV/Vis Spectrometer, Bucks, United Kingdom) at 760 nm. The concentration of total phenolic compounds was determined by comparison with the absorbance of gallic acid 1-hydrate (Panreac, Montplet & Esteban SA, Barcelona, Spain). The total phenolic content was expressed in mg gallic acid per 100 g dry sample. The tannin content was determined reading at 500 nm in the spectrophotometer. The concentration of tannins was estimated by comparison with the absorbance of D-catequine (Sigma, USA). The tannin content was expressed in mg D-catequine per 100 g dry sample. All tests were run in triplicate and averaged.

Statistical Analysis

The study was carried out in three replications (n = 3). Therefore, 3 samples corresponding to different production lot were taken for each crop year. The data were analyzed using the InfoStat software, version 1.1 (Facultad de Ciencias Agropecuarias, Universidad Nacional de Córdoba). Means and standard deviations were calculated. Analysis of variance and the LSD test were used to detect significant differences ($\alpha = 0.05$).

Results and Discussion

Results obtained from the chemical parameters analyzed in the studied residual cakes are shown in Tables 1 and 2. The lipid content was lower in RC 2003 and 2002 (8.62 % and 10.20%, respectively) with second pressing operation than in RC 2001 with single pressing process (13.42%). These results were similar to the ones reported by other authors: 8-10% in RC with second pressing process [1], and 12.3% [11, 12] and 12-18% [1] in RC with first pressing process. The lipid content in the RC presented significant differences ($p < 0.0002$). These variations were attributed to a greater efficiency of wax extraction using a second pressing operation on the jojoba press-cake.

Table 1: Composition of macro component (% w/w on dry base) of residual cakes from jojoba seeds produced in Bañado de Los Pantanos, La Rioja.

Samples	Moisture[1]	Ash[1]	Lipid[1]	Protein[1]	NFE[1,2]
RC 2001	5.01±0.02c	4.08±0.03c	13.42±008c	23.20±0.40a	54.29±0.47a
RC 2002	3.44±0.01a	3.26±0.04a	10.20±0.17b	24.86±0.14a	58.24±0.27c
RC 2003	4.66±0.03b	3.89±0.02b	8.62±0.07a	26.87±0.19b	55.96±0.09b
ANOVA	p<0.0001	p<0.0004	p<0.0002	p<0.011	p<0.0034

[1]Mean ± Standard Deviation (n=3). Different letters in the same column indicate significant differences ($\alpha < 0.05$).
[2]NFE = Nitrogen-free extract.

Table 2: Acid value, peroxide value and p-anisidine value of residual cakes from jojoba seeds produced in Bañado de Los Pantanos, La Rioja.

Samples	Acid Value[1] (mg KOH/g)	Peroxide Value[1] (meq.O_2/ kg)	p-Anisidine Value[1]
RC 2001	6.57±0.25c	4.58± 0.13c	0.80±0.03b
RC 2002	5.11±0.34b	3.65±0.02b	0.75±0.01b
RC 2003	3.22±0.35a	0.98±0.04a	0.22±0.05a
ANOVA	p < 0.011	p<0.0001	p<0.002

[1]Mean ± Standard Deviation (n=3). Different letters in the same column indicate significant differences ($\alpha < 0.05$).

The protein contents in RC were 23.20, 24.86 and 26.87% in 2001, 2002 and 2003 crop years, respectively. Significant differences ($p < 0.011$) were found between RC 2001 - 2002 and RC 2003. Obviously, the protein content increased when the fat content decreased by the pressing process. These percentages were similar to the results found by other authors. These results were 25.60% [12], 25% [13], 26% [11] and 20-25% [1] in RC with first pressing operation and 22-28% in RC with second pressing operation [1]. Other works reported lower protein content in jojoba seeds; these results were 14.91% [3]; 15.20% [14] and 18.87% [15]. The difference in the protein content observed between the jojoba seeds (reported by other authors) and the results of this study was due to the protein content increased when the lipid content decreased because of the wax extraction by pressing in the jojoba residual cake.

The ash content in RC also showed significant differences. RC 2001 had higher ash percentage (4.08%). The RC 2002 exhibited lower ash content (3.26%). Ham *et al.* [11] report 3.76% ash. This value was somewhere between the ash percentages reported in this work.

NFE values varied between 54.29% (RC 2001) and 58.24% (RC 2002). The NFE percentages were higher than the one (45.30%) reported by Zambrano and Cajal [16], from first and second pressing process. The NFE percentages observed in this study were similar to the reported by IJEC for cakes obtained from first and second pressing process.

To characterize the quality of RC resulting from industrial process it is necessary to define limit values of some chemical parameters. Total phenolics, tannin content, and acid, peroxide and p-anisidine values could be used as quality indicator in RC. Polyphenol components are considered compounds with high antioxidant activity but are also considered as anti nutritional factors due to their capacity to precipitate proteins decreasing the bioavailability and nutritional value of such proteins [17]. Fig. 1 presents total phenolics and tannin content of RC. Total phenolics content showed significant differences among crop of years 2001, 2002 and 2003 ($p < 0.001$) and tannin content also showed significant differences between RC 2003 and RC 2001 - RC 2002 ($p<0.02$). The values of these parameters increased with storage time (Fig. 1). It was observed in plant material that phenolics and tannins content increase in death and damage [18]. The highest values were observed in RC 2001. Instead, RC 2003 had the lowest total phenolics and tannin compound content (0.33% and 0.42%).

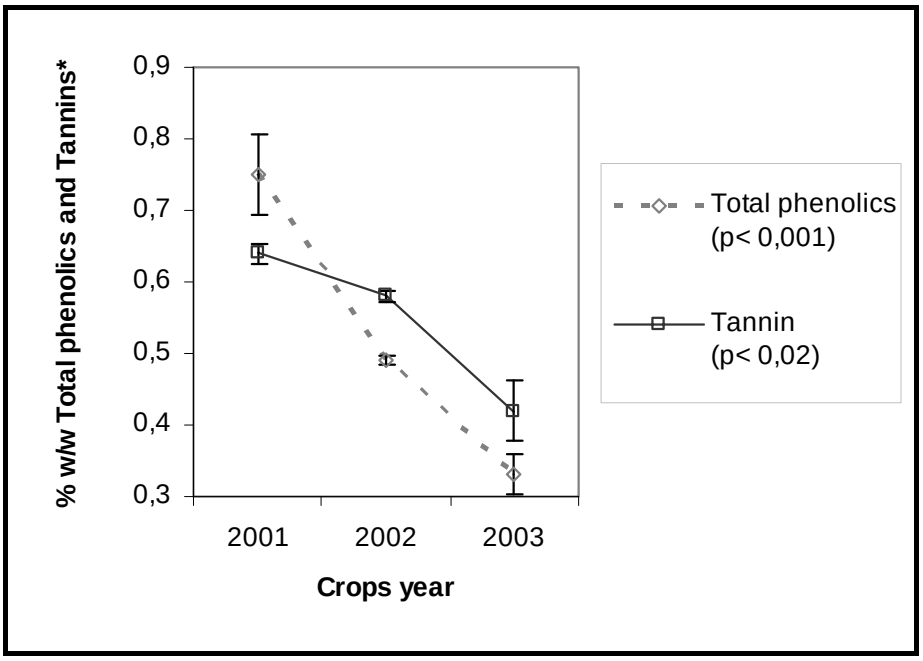

Fig. 1: Total phenolics and tannin content of residual cakes from jojoba seeds produced in Bañado de Los Pantanos, La Rioja.
Mean ± Standard Deviation (n=3).
*%w/w = weight/weight percentage on dry base.

Table 2 presents acid, peroxide and p-anisidine values of RC. Free fatty acids present in the lipids of a sample are measured as acid value. Higher acid value indicates hydrolytic deterioration [19]. Fatty acids linked to long chain alcohols forming fatty alcohols esters. These represent 98% of the jojoba wax composition, whereas, the free fatty acids are found in low quantity [1, 3, 20]. The highest acid values were found in

RC 2001 and RC 2002. In these cases, the hydrolytic processes occurred for the actions of the environmental conditions during *in situ* storage [19]. IJEC [1] allows for an acid value less than 1.0 mg KOH/g wax. Considering this level, the residual wax in RC 2001, RC 2002 and RC 2003 were out of the specified limit in this parameter.

Peroxide value mainly informs about primary oxidation products. The peroxide values from the residual wax obtained from the jojoba press-cakes showed significant differences among different storage years. The highest peroxide value was exhibited by RC 2001. The oxidative deterioration in the lipids due to air contact along the storage time is the main cause for an increase in the peroxide value. There is a direct balanced relation among exposure to air, peroxide values, and the amount of oil in the material [19]. IJEC [1] allows for peroxide value is less than 2 meqO_2/kg wax. Only, RC 2003 had acceptable quality for this parameter. Therefore, RC 2003 could have been used for wax extraction

The assay of p-anisidine is used to measure the degree of secondary oxidation reaction. The p-anisidine values were higher in RC 2001 and RC 2002. Significant differences were found in p-anisidine values between RC 2001-2002 and 2003. The reported p-anisidine values en RC were very low. Ortega-Nieblas, *et al.* [21] observed higher p-anisidine in soy oil (PAV 0.89) after 10 minutes at 180ºC during the frying process. Schnepf, *et al.* [22] also found high p-anisidine values in soy oil (PAV 1.3), fish oil (PAV 16.3) and a mixture (70/30) of both of them (PAV 6.7) after a short storage time. Crapiste *et al.* [19] informed that when sunflower oil was stored for 100 days at 47°C, the p-anisidine value obtained was 82.5. This value is around a hundred times higher than the highest value shown in this work found in RC 2001 (PAV 0.80). The p-anisidine results indicate a strong resistance to lipid oxidation in the jojoba wax.

Table 3: Total phenolics, tannin content, acid value, peroxide value and p-anisidine value of residual cakes obtained for industrial (RC) and laboratory (LC) process harvested in 2003.

Samples	Total phenolics[1] (% w/w)[2]	Tannins[1] (% w/w)[2]	Acid Value[1] (mg KOH/g)	Peroxide Value[1] (meq.O_2/ kg)	p-Anisidine Value[1]
RC 2003	0.33±0.03c	0.42±0.02b	3.22±0.35b	0.98±0.04b	0.22±0.05a
LC 2003	0.30 ± 0.03c	0.40±0.01b	0.46±0.004a	0.40±0.03a	0.10±0.01a
ANOVA	p = 0.55	p=0.46	p<0.015	p<0.007	p=0.14

[1]Mean ± Standard Deviation (n=3). Different letters in the same column indicate significant differences (α< 0.05).
[2]%w/w = weight/weight percentage on dry base.

Table 3 presents total phenolics, tannin contents, and acid, peroxide and p-anisidine values of residual cake obtained for industrial and laboratory process harvested in 2003. Significant differences between RC 2003 and LC 2003 were not detected in total phenolics and tannin content. This indicates that the process and/or the pressing conditions did not affect the content. The wax of jojoba seeds extracted under

cold pressing (LC 2003) showed the lower acid value (0.46 mgKOH/g) than RC 2003. A similar result was found in another work [20]. Significant differences were found in the acid value between RC 2003 and LC 2003 ($p < 0.015$). This difference was caused by the pressing conditions due to industrial pressing in the RC 2003 where pressure and heating were applied on the pressed material. Such factors are responsible for increasing ester hydrolysis [3]. Peroxide values between RC 2003 and LC 2003 were significantly different. Tobares *et al.* [20] reported similar PV (0.39 meq O_2/ kg) in wax obtained by cold pressing process. RC 2003 and LC 2003 did not show significant difference in p-anisidine value. Both values are very low and are acceptable according to the level suggested in IJEC [1].

Conclusions

Residual Cake obtained by pressing of jojoba seed has low fat matter and high protein content. This material could be used as an ingredient for food elaboration which is destined to animal feed; though the simmondsine, anti-nutritional factor, should be previously eliminated from the residual cake.

Residual Cakes produced from the secondary pressing operation have smaller amounts of residual wax and their quality parameters are not altered with respect to RC obtained by a single pressing operation. Long exposure to air and high temperatures due to *in situ* storage, the residual cake of jojoba develops products of lipid oxidation that can be measured by the p-anisidine, peroxide and acid value. This lipid oxidation process can be stopped or decreased if the RC were processed at low temperature and stored in a cold and dark storage. Besides, it would be useful to define what levels of total phenolics, tannin content, acid value, peroxide value and p-anisidina value are acceptable to produce residual cakes of good quality as an ingredient for animal feed.

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