GRASAS Y ACEITES 66 (3)
July–September 2015, e083
ISSN-L: 0017-3495
doi: http://dx.doi.org/10.3989/gya.0954142

Temperature dependence of refractive index and of electrical impedance of grape seed (*Vitis vinifera, Vitis labrusca*) oils extracted by Soxhlet and mechanical pressing

D.S. Vieira[a], M. Menezes[b], G. Gonçalves[c], H. Mukai[a], E.K. Lenzi[a], N.C. Pereira[d] and P.R.G. Fernandes[a,✉]

[a]Departamento de Física, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020 900, Maringá, PR, Brasil
[b]Universidade Tecnológica Federal do Paraná, Rua Marcílio Dias, 635 – Apucarana, PR, Brasil
[c]Departamento de Engenharia Química, Universidade Tecnológica Federal do Paraná, Av. Monteiro Lobato, s/n - Km 04, 84016-210, Ponta Grossa - PR, Brasil
[d]Departamento de Engenharia Química, Universidade Estadual de Maringá, Av. Colombo, 5790, 87020 900, Maringá, PR, Brasil

✉Corresponding author: pricardo@dfi.uem.br

Submitted: 25 September 2014; Accepted: 10 February 2015

SUMMARY: In this report, the temperature dependence of the refractive index and electric impedance of vegetable oil grape seeds extracted from *Vitis vinifera* (v. Cabernet) and *Vitis labrusca* (v. Bordo) are investigated by means of experimental techniques. The seeds were collected from wineries located in two cities in the south of Brazil. In both extraction methods, the seeds were dried at 40.0 °C and at 80.0 °C, respectively, before the oil extraction. From optical microscopy and refractometry results, one can see that the grape seed oil extracted by mechanical pressing shows a linear dependence between the refractive index and temperature and has no birefringent residues. From the fitting of the EIS (Electrical Impedance Spectroscopy) data, an equivalent electric circuit composed of a parallel RC in series with a resistor is proposed. The circuit model is in good agreement with the experimental data and provides the electrical permittivity of the vegetable oils investigated.

KEYWORDS: *Complex Fluids; Electric Circuits; Electrical Impedance; Grape Seed Oils; Refractive Index*

RESUMEN: ***Índice de refracción e impedancia eléctrica en función de la temperatura de aceites de semillas de uva* (Vitis vinifera, Vitis labrusca) *extraídos mediante Soxhlet y prensado mecánico***. Se investiga mediante técnicas experimentales la dependencia del índice de refracción y la impedancia eléctrica de aceites vegetales extraídos de semillas de uva *Vitis vinifera* (v. Cabernet) y *Vitis labrusca* (v. Bordo). Las semillas fueron recolectadas de bodegas situadas en dos ciudades al sur de Brasil. Antes de la extracción del aceite, mediante dos métodos de extracción, las semillas fueron secadas a 40,0 °C y 80,0 °C. De los resultados de refractometria y microscopía óptica, se comprueba que el aceite de semilla de uva extraída por prensado mecánico obedece a una relación lineal del índice de refracción con la temperatura y no presentan resíduos birrefringentes. Con los datos de impedancia eléctrica, se propone un circuito eléctrico equivalente formado por una resistencia y un condensador en paralelo, a su vez ligado a otra resistencia en serie. El modelo de circuito tiene una alta correlación con los datos experimentales y permite obtener la constante dieléctrica de los aceites vegetales investigados.

PALABRAS CLAVE: *Aceites de semillas de uva; Circuitos eléctricos; Fluidos complejos; Impedancia eléctrica; Índice de refracción*

Citation/Cómo citar este artículo: Vieira DS, Menezes M, Gonçalves G, Mukai H, Lenzi EK, Pereira NC, Fernandes PRG. 2015. Temperature dependence of refractive index and of electrical impedance of grape seed (*Vitis vinifera, Vitis labrusca*) oils extracted by Soxhlet and mechanical pressing. *Grasas Aceites* **66** (3): e083. doi: http://dx.doi.org/10.3989/gya.0954142.

1. INTRODUCTION

Great quantities of residues are produced by the wine industry, whose management and disposal are environmental problems due to their seasonal character and some polluting characteristics. The main solid by-products and residues generated are grape stalk, grape pomace or marc, exhausted grape marc winery sludge and seeds (Bustamante *et al*., 2008; Devesa-Murcia *et al*., 2011). The production of grape seed oil is an alternative to use the residue of the wine producing industry. Grape seed oil is rich in linoleic acid (Pardo *et al*., 2009; Freitas 2007; Ahmadi and Siahsar, 2011; Cao and Ito, 2003) and contains great antioxidant power, due to the presence of vitamin E in its composition. One important effect associated with grape and grape-related products is the reduction in bad cholesterol (LDL) and the increase in good cholesterol (HDL), decreasing the risk of cardiovascular disease (Jayaprakasha *et al*., 2001; Nassiri-Asl and Hosseinzadeh, 2009; Viagna *et al*., 2003; Feringa *et al*., 2011). A review about the health benefits associated with grape products including the grapes *Vitis labrusca* and *Vitis vinifera* can be seen in reference (Vislocky and Fernandez, 2010). In addition, grape seed oil is one of the carriers of many essential oils used in various processes of health (Lavabre, 1993) such as therapeutic massage (Jäger *et al*., 1992; Hongratanaworakit, 2011). The percutaneous absorption of the essential oil in the massage oil is increased due to the low viscosity of the grape seed oil used as carrier. However, the absorption of oils through the skin depends on the type of oil being used, the type of carrier and on the temperature of the surrounding air and of the oil itself. In spite of the widespread use of essential oil, little research about its absorption via the skin has been described. In this sense, the investigation of the electrical properties of the grape seed oil as a function of temperature aims to make a contribution to the understanding of the oil absorption process through the skin. In this sense, the Electrical Impedance Spectroscopy (EIS) that has been used in the investigation of ionic solutions (Lenzi *et al*., 2011), can give a good description of the behavior of the electrical impedance as a function of temperature, Z (T) of these carrier oils investigated. Once refractive index n is related to the electric permittivity ε of the studied material (Born and Wolf, 1980), experimental investigation of n as a function of temperature, n (T), is of extreme relevance.

The goal of the present study is to investigate the behavior of n (T) of grape seed oils extracted from the seeds of *Vitis vinifera* (var. Cabernet - Sauvignon) and *Vitis labrusca* (var. Bordo) by mechanical pressing and Soxhlet methods, and to investigate the behavior of Z (T) in these carrier oils from 0.01 Hz to 1.0 MHz.

2. MATERIALS AND METHODS

2.1. Preparation of samples

The vegetable oil samples were prepared from the grape seeds of the varieties *Vitis vinifera* and *Vitis labrusca*, at approximately 100 Kg each. The seeds were collected during the harvest period (November 2010 to March 2011) from wineries located at two cities in the south of Brazil. The transportation was done in closed coolers to the Laboratory of Separation Processes of the Universidade Estadual de Maringá. Before oil extraction, the seeds were sieved out from waste, washed in deionized running water and then in hot water (~100.0 °C) in order to remove husks, stalks and sugar as cited in Freitas (2007). After cooling down to room temperature, the seeds were packed in plastic bags and stored at −15.0 °C. For both extraction methods, the seeds were dried, respectively, at 40.0 °C and 80.0 °C.

2.2. Drying process

In order to dry the seeds a convective drying with transversal flux was used. The seeds were dried at 40.0 °C and at 80.0 °C with an air flux speed of 0.8 m/s. The flux was controlled by means of a digital anemometer (TAVR-650). Before each oil extraction the seeds were ground in a grinder (model TE-345) for 10 seconds, homogenized and milled for another 10 seconds. When the desired drying was reached the mass of seed was measured using an analytical balance (GEHAKA-Bg 4000, 0.01 g of precision). The measurements of mass were made with an interval of one minute during 30 minutes. After this time the interval between two consecutive measurements of mass was two minutes. The humidity of the seeds was evaluated using Equation (1).

$$X_{db}(t) = \frac{M(t) - M_d}{M_d} \tag{1}$$

where $X_{db}(t)$ is the humidity as a function of time in dry base, $M(t)$ is the mass of seeds in the instant t, M_d is the mass of drying seeds.

2.3. Extraction processes

In order to extract the oil two methods were used. One of them was the cold pressing and other one was the Soxhlet process. In the cold pressing a Bovenau press (capacity of 30 ton) was used. The extraction was made using 14 tons of pressure, during 12 h, on 100 g of grape seeds previously cleaned, dried and milled. The sizes of milled particles were found between 11.7 μm and 83.3 μm. The extraction cell was a stainless steel cell made in the mechanical laboratory of UEM (University of Brazil). In the Soxhlet process the solvent was dichloromethane and the extraction was made, for at least 4 h, at the melting point. In this method, the extraction was made with 10 g of seeds previously cleaned, dried and milled in 300 mL of solvent.

2.4. Moisture content

After extracting the oil from seeds dried at 40.0 °C and 80.0 °C the moisture content was determined using the Karl Fisher (Analyser, KF-1000) method. The relative humidity in oils was found between 0.22% and 0.52% considering both extraction methods, drying temperatures and types of grape. The maximum value was found for oil extracted by pressing *V. vinifera* seeds dried at 40.0 °C. The minimal value was found for oils extracted by pressing *V. labrusca*.

2.5. Composition of fatty acids

In order to determine the composition of fatty acids of the grape seed oil a gas chromatograph Varian, CO-3800 was used. To quantify the methyl ester, the standard methodology used by Visentainer and Franco (Visentainer and Franco, 2006) was followed. The standard methyl ester from tricosanoic acid (99%) was from Sigma-Aldrich. The fatty acid compositions of the oils extracted are shown in Tables 1 and 2.

Table 1. Percentage composition of fatty acids of oils obtained from grape seeds dried at 40.0 °C

	V. labrusca (var. Bordo)		*V. vinífera (var. Cabernet Sauvignon)*	
Fatty acids	**Press (%)**	**Soxhlet (%)**	**Press (%)**	**Soxhlet (%)**
14:0	0.05	0.08	0.07	0.08
16:0	6.49	6.84	7.25	7.99
16:1n-9	0.04	0.04	0.05	0.05
16:1n-7	0.11	0.15	0.11	0.14
17:0	0.04	0.05	0.05	0.06
18:0	3.07	3.22	3.54	3.79
18:1n-9	16.76	17.68	13.01	13.98
18:1n-7	0.62	0.68	0.55	0.61
18:2n-6	66.06	65.25	68.76	66.81
18:3n-3	0.42	0.49	0.04	0.04
20:0	0.14	0.16	0.16	0.18
20:1n-9	0.15	0.16	0.13	0.14
22:0	0.02	0.03	0.03	0.05

Table 2. Percentage composition of fatty acids of oils obtained from grape seeds dried at 80.0 °C

	V. labrusca (v. Bordo)		*V. vinifera (v. Cabernet Sauvignon)*	
Fatty acids	**Press (%)**	**Soxhlet (%)**	**Press (%)**	**Soxhlet (%)**
14:0	0.06	0.06	0.07	0.07
16:0	6.41	6.52	7.49	8.02
16:1n-9	0.04	0.04	0.04	0.06
16:1n-7	0.11	0.12	0.11	0.13
17:0	0.04	0.04	0.03	0.03
18:0	2.97	3.09	3.42	3.86
18:1n-9	16.72	16.44	12.58	13.83
18:1n-7	0.62	0.62	0.57	0.58
18:2n-6	66.06	63.65	69.37	66.57
18:3n-3	0.40	0.41	0.39	0.41
20:0	0.14	0.15	0.15	0.17
20:1n-9	0.13	0.12	0.10	0.11
22:0	0.02	0.03	0.03	0.05

2.6. Polarized optical light microscopy (POLM)

A polarizing microscope (Leica DM 2500) with a camera (Leica DFC290) attached was used in order to analyze the birefringence of the oil samples. The POLM technique consists of observing a thin film sample between crossed polarizers. This is one standard technique applied in the investigations of anisotropic fluids such as liquid crystal (Mukai *et al*., 2007). When the light passes through the birefringent sample, it suffers modification in its polarization plane due to the optical anisotropy of the material, which in turn reveals the typical textures of each sample. If the sample is optically isotropic no light passes through the sample resulting in a dark texture. In this work the oils samples were placed in a capillar glass of 200 μm thickness. The optical analysis of the samples was made by rotating the platinum of the microscope in three different angles: 0°, 45° and 90° with respect to the polarization direction of the polarizer. The optical textures were obtained at room temperature and were observed by using the software *Infanview*.

2.7. Refractometry

Refractometry is an experimental technique widely used in the study of anisotropic fluids such as liquid crystals (Kimura *et al*., 2004) and composites formed by hydrogel doped with liquid crystal (Aouada *et al*., 2004). In this work, the refraction index of the oils was measured using an ABBE refractometer model Atago RX 5000α. The refractometer possesses a complete scale, ranging from 1.32700 to 1.58000 with a precision of 0.2% and a BRIX from 0–100.00% with a precision of 0.03%. The refractometer has a thermostat which allows for reading temperatures from 5.0 °C to 60.0 °C. In this work, the analysis temperature range used was from 16.0 °C to 50.0 °C. In order to avoid spurious impurities in the sample, care was taken with cleaning the refractometer. The cleaning was done with a solution of water and detergent (50%). This solution was applied onsite and removed carefully with a cotton swab to avoid risks of onsite measurements. After this, the excess solution was removed with a highly absorbant paper. This cleaning procedure was repeated three times. After the cleaning procedure, calibration was made by measuring the refractive index of distilled water at 20.0 °C. After calibration, 0.01 mL of oil sample was placed in the base of the refractometer and the refraction index of the oil was measured as a function of temperature.

2.8. Electrical impedance spectroscopy (EIS)

A Solartron 1260A impedance-gain phase analyzer was used in order to measure the real *R (f)* and imaginary Im (f) parts of the electrical impedance *Z (f)* of the grape seed oils. The frequency range used was from 0.01 Hz to 1.0 MHz. The amplitude of the AC applied voltage was 1.0 V. The sample (V=15 mL) was placed between two circular plates of stainless steel with an area of 3.14 cm^2 and thickness of 0.1 mm. The thickness was controlled with a digital micrometer attached to the sample holder 12962 of the Solartron analyzer. The electrodes were cleaned with the following procedure: first, the electrodes were washed with detergent and deionized water. After that, the electrodes were polished with fine sandpaper. Finally, the electrodes were placed in an ultrasonic bath at 40 KHz for 10 min. The temperature sample was controlled with a thermostatically controlled water bath with a stability of 0.01 °C. The automated data acquisition was carried out by means of a computer equipped with *ZPlot* software from Solartron Analytical. In the frequency range from 0.01 Hz to 1 MHz, each value of impedance in their specific frequency is a simple mean of five consecutive measurements. In order to ensure reproducibility, the entire procedure was repeated three times with twenty minutes between each one. The reproducibility was obtained with a maximum deviation of about of 0.01%.

3. RESULTS AND DISCUSSION

3.1. Composition of fatty acids and moisture content

By using grape seeds of *Vitis vinifera* dried at 40.0 °C and 80.0 °C, the extracted oil content was 6% and 3% at each respective temperature when apply the pressing extraction method. When the Soxhlet process was applied, the content of extracted oil was 20% and 16% for the same drying temperatures. When the grape seeds of dried *Vitis labrusca* at 40.0 °C and 80.0 °C were used, the oil content was, respectively, 8% and 4% after applying the pressing method and 12% and 14% after applying the Soxhlet method. Each oil sample was analyzed using gas chromatography, and the presence of linoleic acid as the principal compound of the oil was confirmed. The percentage composition of fatty acids of the oils extracted for both extraction methods are shown in Tables 1 and 2 for drying temperatures of 40.0 °C and 80.0 °C, respectively.

Table 3. Moisture content for each kind of grape seed

Extraction Method	Variety	Drying temperature (°C)	Moisture content (%)
Soxhlet	*V. vinifera*	40.0	0.300
Soxhlet	*V. vinifera*	80.0	0.260
Soxhlet	*V. labrusca*	40.0	0.346
Soxhlet	*V. labrusca*	80.0	0.204
Press	*V. vinifera*	40.0	0.321
Press	*V. vinifera*	80.0	0.256
Press	*V. labrusca*	40.0	0.235
Press	*V. labrusca*	80.0	0.221

Considering the deviation measurements in the chromatography technique there are no significant differences among fatty acids for both extraction methods. This shows that the temperature of seed drying and extraction method did not significantly influence the quality of the extract oil. All oils had high fatty acid contents (>81%). The chemical composition of the extracted oil contains essentially oleic, linoleic, palmitic and stearic fatty acids. This composition is in agreement with the mean composition of grape seed oil (Freitas, 2007). Table 3 shows the moisture contents of the grape seed oils extracted with pressing and Soxhlet methods at 40.0 °C and 80.0 °C drying temperatures. The values for moisture content in Table 3 confirm the expected results: increasing the drying temperature causes a decrease in the moisture content in the oil. For comparison, the moisture content in soybean oil, for example, is limited to up to 0.5% which is the maximum amount recommended so as not to harm the transesterification process.

3.2. Polarized optical light microscopy (POLM)

In order to study the effective birefringence of the extracted oils by means of two different methods of extraction, the Polarized Optical Light Microscopy (POLM) technique was applied. Figures 1, 2, 3 and 4 show typical POM micrographs from the

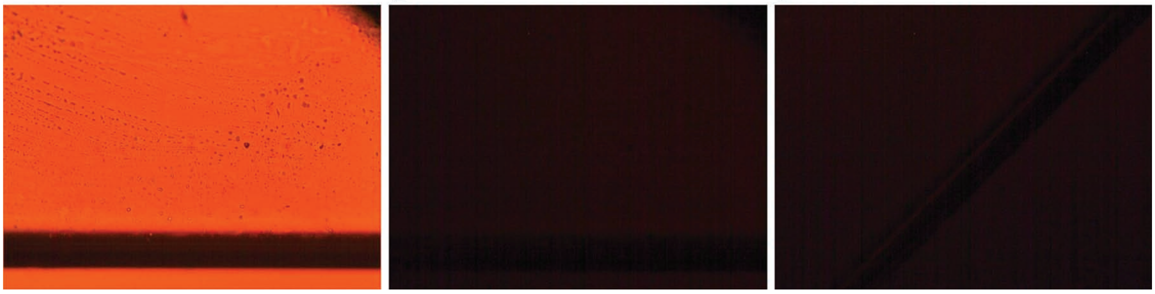

FIGURE 1. Optical textures of grape seed oil from *Vitis labrusca* (v. Bordo) extracted by mechanical press after drying at 80.0 °C; Optical measurements made at 27.4 °C; (A) θ=0°; (B) θ=90°; (C) θ=45°; Figure scale: 1 cm=200 μm.

FIGURE 2. Optical textures of grape seed oil from *Vitis labrusca* (v. Bordo) extracted by Soxhlet after drying at 80.0 °C; Optical measurements made at 27.4 °C; (A) θ=0°; (B) θ=90°; (C) θ=45°; Figure scale: 1 cm=200 μm.

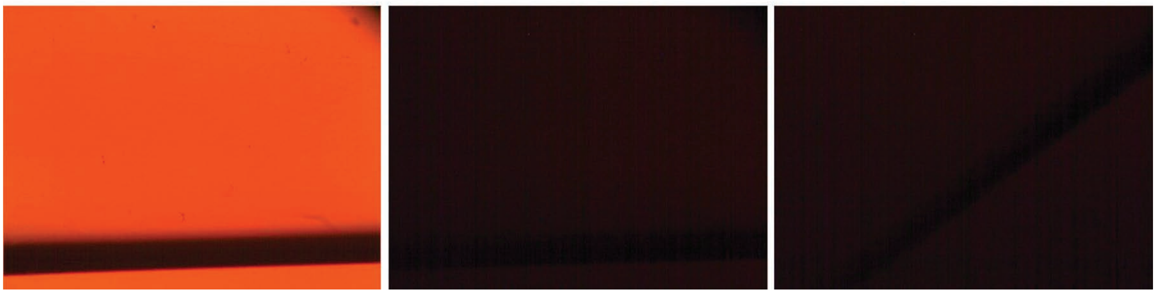

FIGURE 3. Optical textures of grape seed oil from *Vitis vinifera* (v. Cabernet) extracted by mechanical press after drying at 80.0 °C; Optical measurements made at 27.4 °C; (A) θ=0°; (B) θ=90°; (C) θ=45°; Figure scale: 1 cm=200 μm.

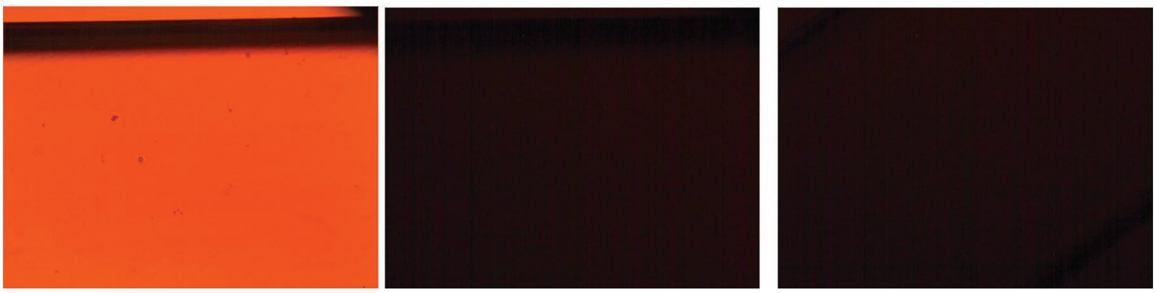

FIGURE 4. Optical textures of grape seed oil from *Vitis vinifera* (v. Cabernet) extracted by Soxhlet after drying at 80.0 °C; Optical measurements made at 27.4 °C; (A) θ=0°; (B) θ=90°; (C) θ=45°; Figure scale: 1 cm=200 μm.

grape seeds oils of *Vitis labrusca* and *Vitis vinifera* when dried at 80.0 °C and extracted by pressing and Soxhlet methods. The optical textures, magnified by 100x, were obtained by placing the sample between crossed polarizers. The micro slide containing the sample was rotated in three different angles, 0°, 45° and 90°, with respect to polarization direction of the polarizer. It can be observed that the textures obtained for the oils extracted by pressing are typical of isotropic systems (Figures 1b and 1c) whose optical anisotropy (birefringence) is null. On the other hand, the optical textures of the grape seed oils extracted by the Soxhlet method show birefringent dots (identified by bright spots in Figures 2b and 2c). These birefringent regions are associated with the existence of anisometric particles in the oil. These particles are probably some few remains of the solvent used in the extraction by Soxhlet. In order to reduce the birefringent dots when using the Soxhlet method two ways are possible: increasing the drying temperature for both kinds of grape seeds or using *Vitis vinifera* grape seeds (see Figures 3 and 4) at any drying temperature used in this work. In this way, it is shown that the oils extracted from *Vitis vinifera* grape seeds are not influenced by the extraction method. Furthermore, a high drying temperature reduces the moisture in the seeds, thus contributing to the reduction in the amount of waste in the extracted oils.

3.3. Refractometry

The effective refractive indexes of the oils studied in this work were measured in an ABBE refractometer. Figures 5 and 6 show refractive index as a function of temperature, n (T), of the oils extracted from the seeds of *Vitis labrusca* (Figure 5) and *Vitis vinifera* (Figure 6) by means of Soxhlet (circles) and mechanical pressing (triangles) for seeds dried at 40.0 °C (black symbols) and 80.0 °C (gray symbols). The range of temperature used in these measurements was from 16.0 °C to 50.0 °C. As can be seen, n (T) decreases linearly with respect to temperature for both types of grape and for different drying temperatures of seeds. However, only with the pressing method is the linear behavior of n (T) reversible with temperature. By using the Soxhlet extraction method with *Vitis labrusca* grape seeds, a non-reversible behavior with respect to temperature and non-linearity of n (T) is observed (Figure 7). This non-linearity in n (T) can be associated with the presence of anisotropic particles in shape observed by the POLM technique. Anisotropic particles were not observed in the oils extracted by pressing. In general, one can see that the values of the refractive index for all the oils studied in this work are between 1.46200 and 1.47800. This value range of n (T) is higher than that obtained with grape seed oil extracted from the main Turkish wine grape cultivars (Baydar *et al.*, 2007). In this work, the reproducibility of the measurements of n (T) was checked and deviations were less than 0.1%.

3.4. Electrical impedance spectroscopy (EIS)

The real *R (f)* and imaginary *Im (f)* parts of the electrical impedance, *Z (f)*, of the grape seed oils were performed using the EIS technique. Figure 8 shows the di-log plot of *R (f)* at 20.0 °C of the

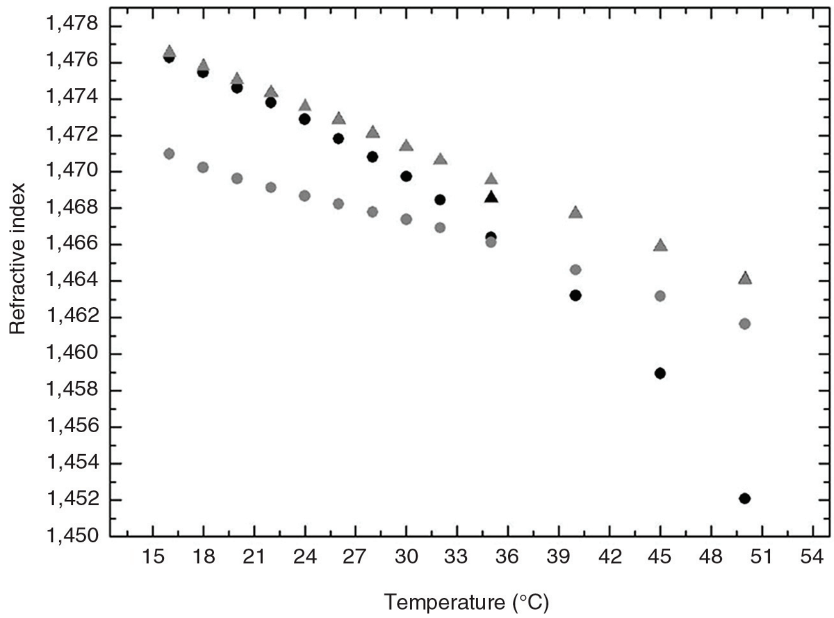

FIGURE 5. Refractive index as a function of temperature; *Vitis labrusca* grape seed oil extracted by Soxhlet (circle) and pressing methods (triangle); Black symbols indicate drying temperatures at 80.0 °C and gray symbols at 40.0 °C.

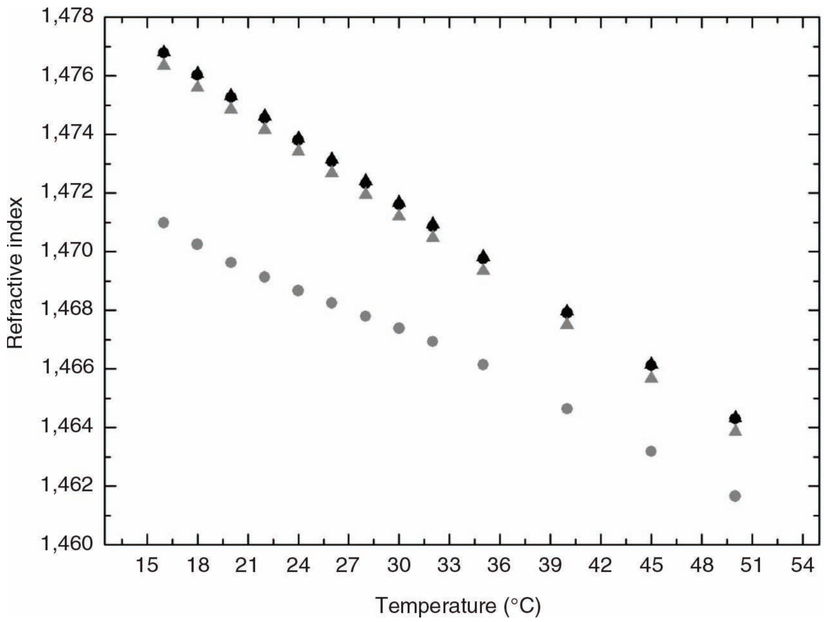

FIGURE 6. Refractive index as a function of temperature; *Vitis vinifera* grape seed oil extracted by Soxhlet (circle) and pressing method (triangle); Black symbols indicate drying temperatures at 80.0 °C and gray symbols at 40.0 °C.

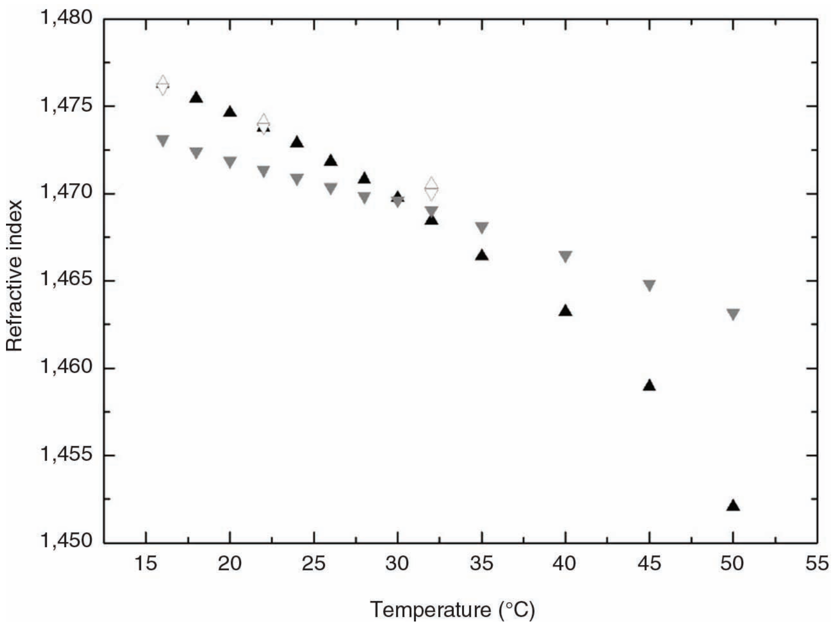

FIGURE 7. Non-reversible (triangles down) and non-linear (triangles up) behavior of refractive index as a function of temperature of *Vitis labrusca* grape seed oil extracted by Soxhlet; Filled triangles indicate heating and empty triangles indicate cooling; Triangles up indicate drying seeds at 80.0 °C and tringles down indicate drying seeds at 40.0 °C.

Vitis labrusca (v. Bordo) grape seed oil extracted by the mechanical pressing (open triangle) and Soxhlet methods (filled circle). Figure 9 shows the di-log plot of *Im (f)* at 20 °C of the *Vitis labrusca* grape seed oil extracted by the mechanical pressing (open triangle) and Soxhlet methods (filled circle). The seeds were dried at 40.0 °C. In both Figures 8 and 9 the continuous line is the best fit for the electrical circuit model of Figure 10 that will be discussed in section 3.4.1.

As expected in the frequency range from 10 mHz to 500 KHz, *R (f)* presents typically two plateaus

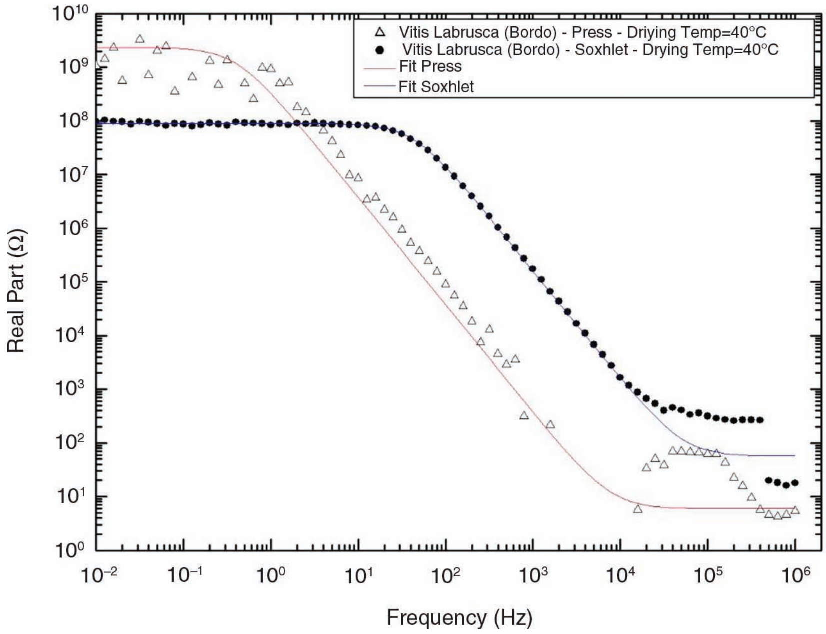

FIGURE 8. Di-log plot of the real part of the electrical impedance of grape seed oils extracted by mechanical pressing and Soxhlet methods. Experimental data obtained at 20.0 °C. The seeds were dried at 40.0 °C; Continuous line is the fit of the electrical circuit model.

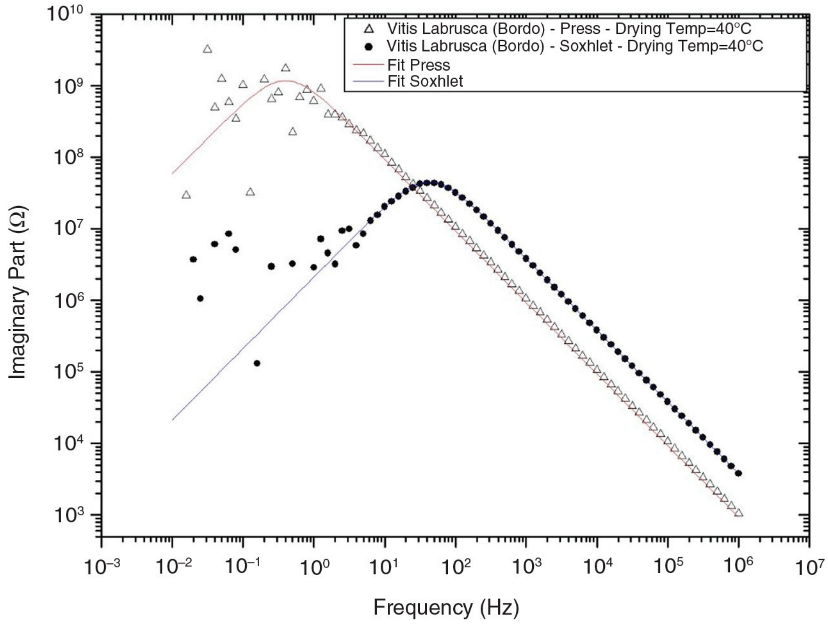

FIGURE 9. Di-log plot of the imaginary part of the electrical impedance of grape seed oils extracted by mechanical pressing and Soxhlet methods. The seeds were dried at 40.0 °C. Experimental data obtained at 20.0 °C. Continuous line is the fit of the electrical circuit model.

connected with a linear decreasing between them. Some great differences have been observed between the Soxhlet and mechanical pressing extraction methods. The first one was the reduction of two orders of magnitude in the value of *R (f)* at a low frequency range when the Soxhlet method was used in comparison with mechanical pressing using the same grape. Another one is the shift in frequency of the maximum of *Im (f)* of one order of magnitude when the Soxhlet process is used. By fixing

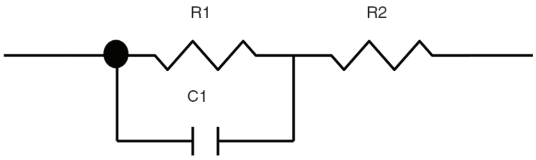

FIGURE 10. Sketch of equivalent electrical circuit used to fit the electrical impedance of oils extracted by Soxhlet and press extraction methods; R1 and R2 are electrical resistors; C1 is a capacitor.

the Soxhlet method one can see that the kind of grape can produce a shift in the maximum *Im (f)* ranging from 200 Hz using *Vitis labrusca* (v. Bordo) to 400 Hz with *Vitis vinifera* grapes. The mechanical pressing does not produce significant shifts in the maximum of *Im (f)* when the type of grape is changed. As another difference between extraction methods is the width of first plateau of *R (f)* of two orders of magnitude lower when the Soxhlet is used. And, finally, as the last difference, a great reduction in the gap of the real part of impedance was observed when the Soxhlet method was used in the frequency region higher than 600 KHz.

Figures 11 and 12 show Nyquist diagrams for the oils (at 20.0 °C) extracted by Soxhlet (filled symbol) and mechanical pressing (open symbol) for both kinds of grapes (*Vitis vinifera* and *Vitis labrusca*) and for different drying temperatures. Continuum lines are the best fits obtained from the electrical circuit model (Figure 10). Figures 11 and 12 show clearly that, for both kinds of grapes, the real part of impedance decreases when the drying temperature is increased, and the oils extracted by mechanical pressing cannot be described by the simple RC circuit. This circuit model is in good agreement with the experimental data only for the oils extracted by Soxhlet. Table 4 show the best fit parameters for the circuit model applied in this paper. By using the dimensions of capacitor and capacitance from the best fit of model the electrical permittivity ε was evaluated. As can be seen in Table 4, only the values for the oils from *V. labrusca* seeds ε change drastically when the temperature for drying the seeds is changed. The ε of the oils from *V. vinifera* seeds have practically the same value when they are extracted by mechanical pressing.

Figures 13 and 14 show complex-plane plots of electrical impedance for temperatures from 16.0 °C to 50.0 °C of the grape seed oils extracted from *Vitis labrusca* (var. bordo) by mechanical pressing with seeds dried at 40.0 °C and 80.0 °C, respectively. Figures 15 and 16 show complex-plane plots for the oil extracted from *Vitis vinifera* (var. Cabernet) in the same conditions of preceding figures. With the exception of Figure 13, in which the oil was extracted by pressing from the seeds of *Vitis labrusca* dried at 40.0 °C, Nyquist diagrams for the mechanical pressing method has shown no semi-circle. An interesting result was noted in the complex-plane plots for both kinds of grapes for the oils extracted by mechanical pressing. All curves show a tendency toward the right side for seeds dried at 80.0 °C while for seeds dried at 40.0 °C this tendency goes to left side (see inset of Figure 15). This unexpected behavior can be

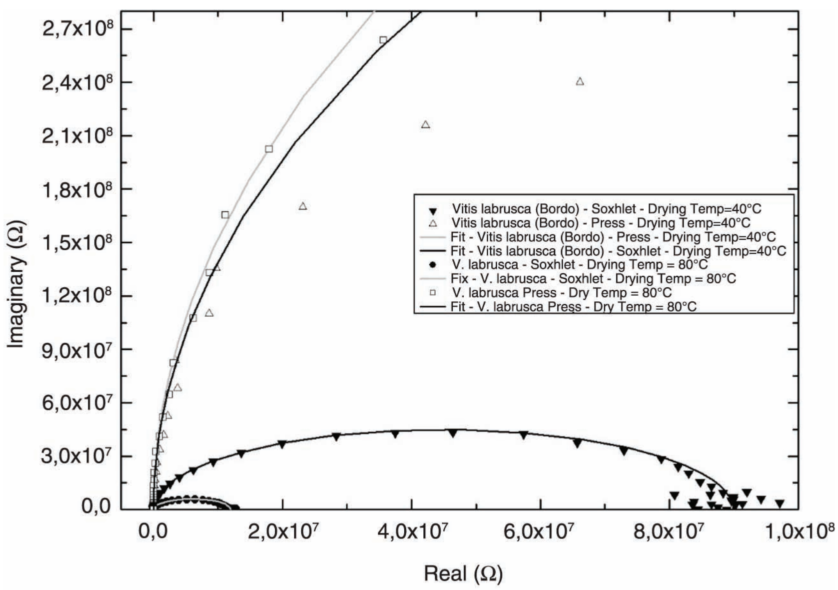

FIGURE 11. Nyquist diagram for oils (at 20.0 °C) extracted by Soxhlet (filled symbol) and mechanical pressing (open symbol) with grape seeds of *Vitis labrusca (Bordo)* dried at 40.0 and 80.0 °C. Continuous lines are the best fits obtained from the electrical circuit (Figure 9). The inset line indicates the region from which the circuit model diverges from the experimental data of oils extracted by mechanical pressing.

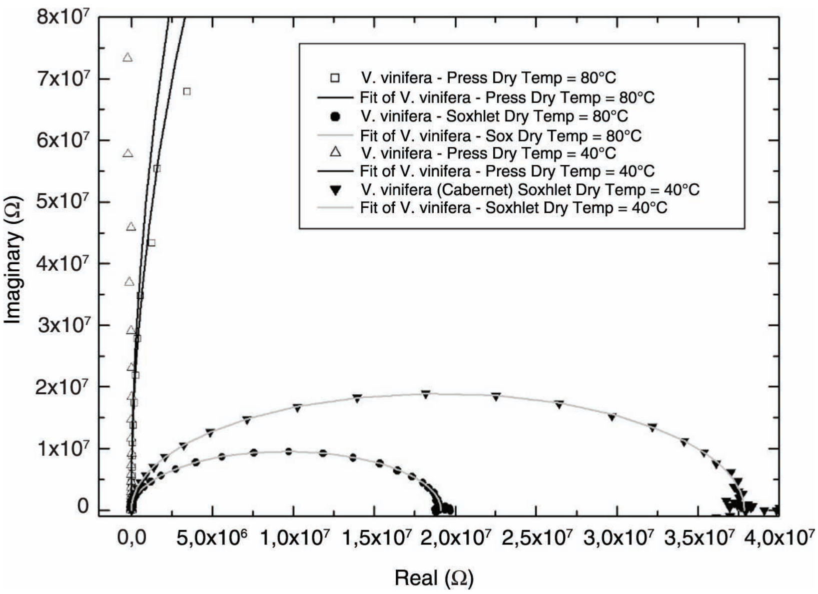

FIGURE 12. Nyquist diagram for oils (at 20.0 °C) extracted by Soxhlet (filled symbols) and mechanical pressing (open symbols) with grape seeds of *Vitis vinifera* (Cabernet) dried at 40.0 °C and 80.0 °C. Continuous lines are the best fits obtained from the electrical circuit model (Figure 9).

TABLE 4. Best fit parameters of the electrical circuit applied to electrical impedance of oils (at 20.0 °C) extracted by the Soxhlet and mechanical pressing methods with grape seeds (*Vitis vinifera* and *Vitis labrusca*) dried at 40.0 and 80.0 °C . The last column shows the electrical permittivity obtained from fit parameters

Extraction Method	Kind of grape seed	Drying Temperature (°C)	Fitting parameters obtained with equivalent electrical circuit fitted to experimental data at 20 °C			Electrical Permittivity
			$R_1(\Omega)$	$C_1(F)$	$R_2(\Omega)$	$\varepsilon = \frac{C_1}{A} d$
Soxhlet	*Vitis labrusca* (Bordo)	40	8.98×10^{7}	4.18×10^{-11}	56.99	1.50419
		80	1.17×10^{7}	2.42×10^{-10}	4.02	8.70848
	Vitis vinifera (Cabernet)	40	3.78×10^{7}	3.46×10^{-11}	91.62	1.24510
		80	1.9×10^{7}	8.09×10^{-11}	50.69	2.91122
Mechanical Pressing	*Vitis labrusca* (Bordo)	40	2.34×10^{9}	1.70×10^{-10}	5.96	6.11753
		80	1.95×10^{9}	4.82×10^{-11}	55.95	1.73450
	Vitis vinifera (Cabernet)	40	2.76×10^{9}	3.95×10^{-11}	110.4	1.42143
		80	1.96×10^{9}	4.35×10^{-11}	90.32	1.56537

associated with higher moisture content (see Table 3) in all the oils extracted by mechanical pressing. By using the Soxhlet extraction method the Nyquist diagrams show a semi-circle for both drying temperatures. For both extraction methods electrical resistance decreases with increasing temperature (see Figures 16 and 17).

3.4.1. *Analysis of the experimental data by means of equivalent electrical circuit*

The electrical behavior of the vegetable oils was investigated by means of an equivalent electrical circuit formed by one parallel R_1C_1 in series with a resistance R_2 (see Figure 10). In this model R_1C_1 is assumed as the resistance and the capacity of the bulk of the sample and R_2 is assumed as a series resistance proper to the surfaces of the capacitor and to the sample near the surfaces of the plates of the capacitor. The values of R_1 and C_1 were obtained from the best fit of the circuit model adjusted to the experimental data. Electrical permittivity of vegetable oils was evaluated from C_1 values and from the characteristics of the cell ($A=3.14\times10^{-4}$ m^2 and $d=1.0\times10^{-3}$ m). In order to fit the electrical impedance of the oils used in this work an RC electrical circuit model (Figure 10) was used. The total electrical

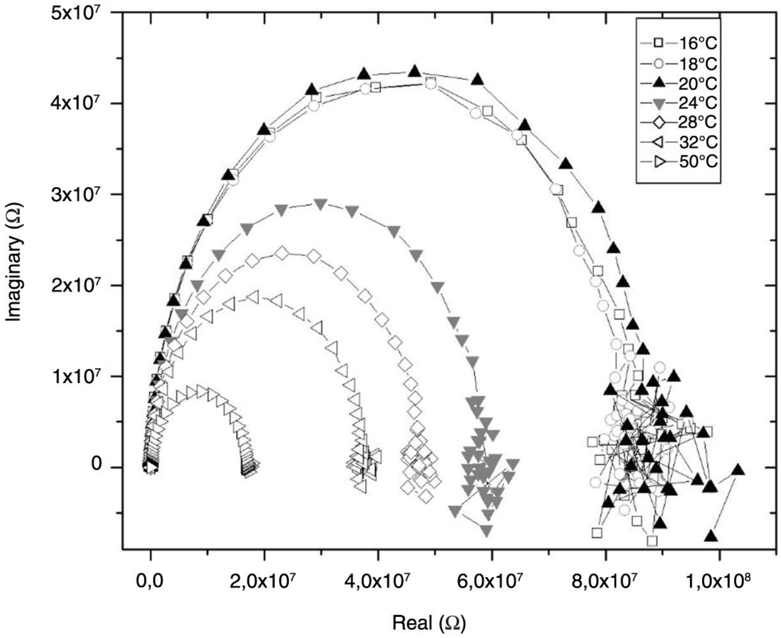

FIGURE 13. Nyquist diagram as a function of temperature. Oil extracted from *Vitis labrusca* (v. Bordo) by mechanical pressing with seeds dried at 40.0 °C.

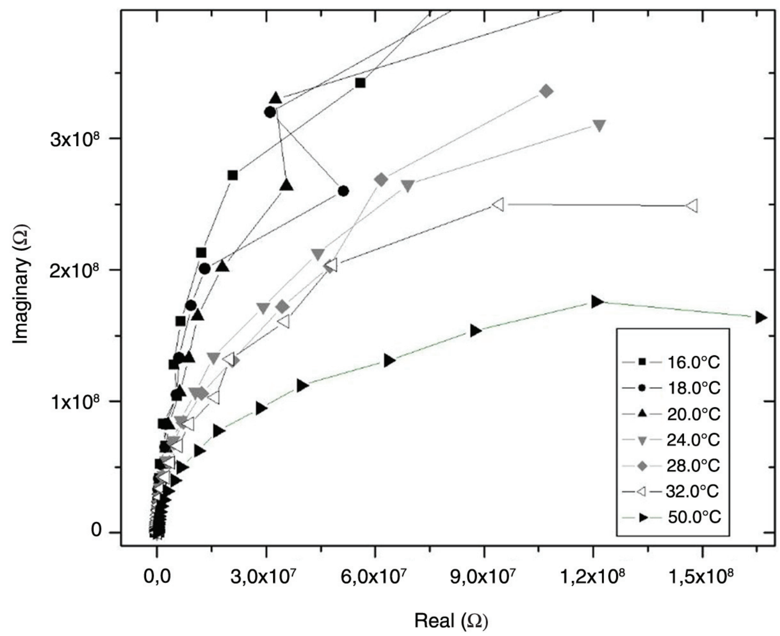

FIGURE 14. Nyquist diagram as a function of temperature. Oil extracted from *Vitis labrusca* (v. Bordo) by pressing with seeds dried at 80.0 °C.

impedance of the circuit model can be written as: $Z_T=Z_1+Z_2$, where

$$Z_1 = \frac{R_1}{1+(R_1\omega C_1)^2} - i\frac{R_1^2\omega C_1}{1+(R_1\omega C_1)^2}$$

with $i=\sqrt{-1}$ and $\omega=2\pi f$.

Z_1 is associated with the electrical impedance of the bulk and $Z_2=R_2$ is a resistance due to electrical contacts and the region of sample near them. Table 4 shows the values of the parameter for the best electrical impedance fitting by using the electrical circuit shown in Figure 10. Only for the oils

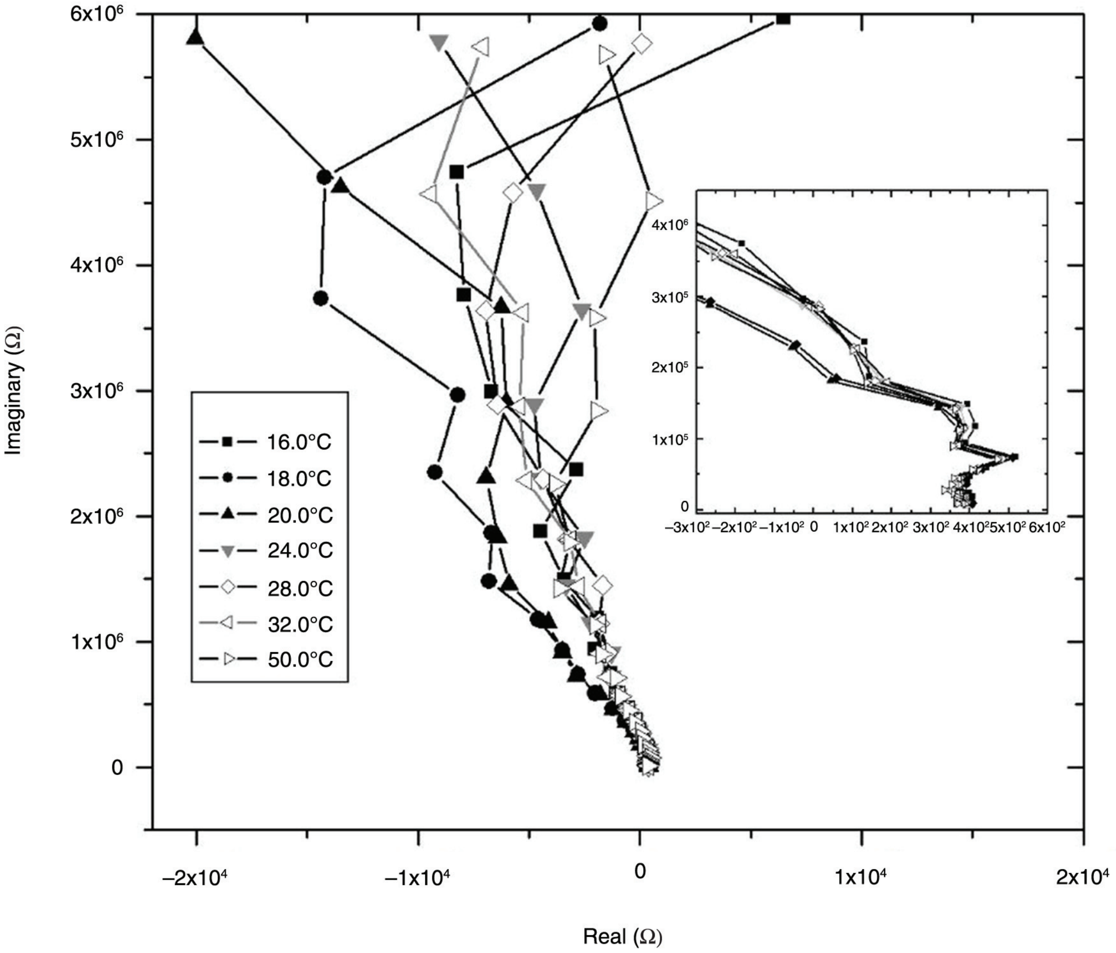

FIGURE 15. Nyquist diagram as a function of temperature. Oil extracted from *Vitis vinifera* (v. Cabernet) by pressing with seeds dried at 40.0 °C.

extracted by Soxhlet process with *Vitis labrusca* grape seeds dried at 80.0 °C was it not possible to obtain reproducibility of measurements or a good fit with one of them. This implies that the Soxhlet method somehow affects the electrical behavior of the oil extracted from *Vitis labrusca* when the seeds are dried at a high temperature. This was one limitation of the Soxhlet method when comparing the two methods of extraction used in this work.

4. CONCLUSIONS

In this work the refractive index and electric impedance of grape seed oils from *Vitis vinifera* and *Vitis labrusca* when extracted by mechanical pressing and Soxhlet methods were investigated. For the mechanical pressing extraction method the refractive index of oils from *Vitis vinifera* (var. Cabernet) and *Vitis labrusca* (var. Bordo) grape seeds showed a typical linearity. However, when the Soxhlet method was applied with *V. labrusca* grape seeds a non-linear behavior in the refraction index is clearly noted. By using the Soxhlet extraction methods a large amount of residual particles was observed due to the solvent used for the extraction. However, we found that these particles can be reduced by increasing the drying temperature of seeds. At a high temperature the moisture of the seeds is reduced and the process of solvent evaporation is favored. Therefore, a consequence of increasing the drying temperature of seeds is the reduction in the amount of waste in the extracted oils by Soxhlet. So, in order to produce oil without residual particles the mechanical pressing method is the best one.

Electrical impedance show good reproducibility for all the extraction processes except when using the *V. labrusca* (var. Bordo) seeds with the Soxhlet method. This implies a disadvantage to using the Soxhlet extraction method to obtain carrier oils. For practical purposes, an equivalent circuit model composed by a parallel RC in series with a resistor was proposed. The electrical impedance of the model is in good agreement with the experimental data.

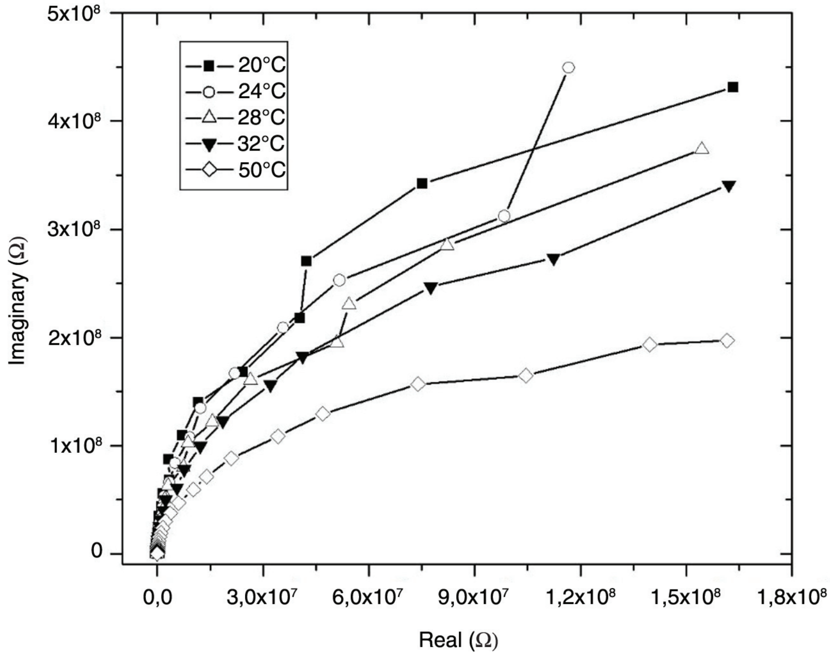

FIGURE 16. Nyquist diagram as a function of temperature. Oil extracted from *Vitis vinifera* (Cabernet) by pressing with seeds dried at 80 °C.

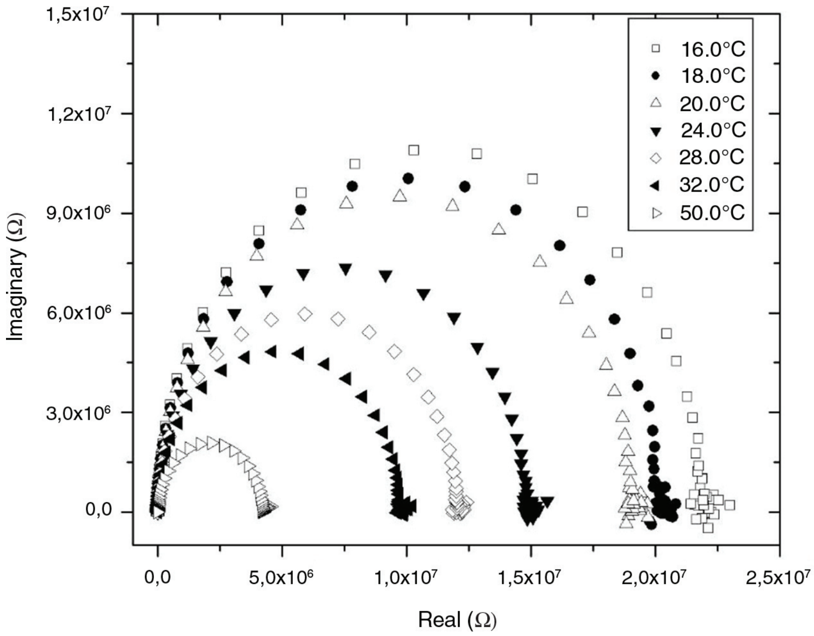

FIGURE 17. Nyquist diagram as a function of temperature. Oil extracted from *Vitis vinifera* (Cabernet) by Soxhlet with seeds dried at 80 °C.

Values of ε of the oils investigated were obtained. This parameter shows no significant differences, only for the oils extracted by mechanical pressing. The values of n obtained from ε have no great discrepancies from those obtained from refractometry, indicating the validity of the circuit model.

To sum up, the experimental results obtained from experimental techniques such as EIS, POLM and refractometry indicate that carrier oils extracted from *Vitis vinifera* grape seeds by mechanical pressing can be more appropriate for therapeutic massage in comparison to oils extracted by Soxhlet.

ACKNOWLEDGMENTS

This work was supported by the National Institute of Science and Technology of Complex Fluids (INCT-FCx/CNPq). We also thank Fundação Araucária (Brazilian Agency). Special thanks are dedicated to A.C. Hablitzel for the suggestions and warm discussions.

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