

Chemical characterization and oxidative stability of olive oils extracted from olive trees of Southern Brazil

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Abstract – The objective of this work was to characterize the chemical composition of olive (*Olea europaea*) oils produced in Southern of Brazil and correlate it with oxidative stability. Olive oils from the Arbequina, Coratina, Frantoio and Koroneiki cultivars were evaluated. A completely randomized experimental design was used, in a uniform arrangement, with three replicates. Acidity value, peroxide index, specific absorption, tocopherol content, phenolic compound content, carotenoid content, chlorophyll content, fatty acid profile, and oxidative stability were determined. The oils from the Coratina and Frantoio cultivars were classified as extra virgin-oils. The olive oil from the Coratina cultivar showed the highest levels of pigments, followed by the oil from Koroneiki. The oil from the Coratina cultivar also presents higher contents of phenolic compounds (1,725.5 mg kg⁻¹) and tocopherols (437.8 mg kg⁻¹). The major fatty acid in all samples is oleic acid.

Index terms: *Olea europaea*, bioactive compounds, fatty acids, induction period, olive, quality parameters.

Caracterização química e estabilidade oxidativa de azeites extraídos de oliveiras do Sul do Brasil

Resumo – O objetivo deste trabalho foi caracterizar a composição química de azeites de oliva (*Olea europaea*) produzidos no Sul do Brasil e correlacioná-la com a estabilidade oxidativa. Foram avaliados azeites das cultivares Arbequina, Coratina, Frantoio e Koroneiki. Utilizou-se o delineamento experimental inteiramente casualizado, em arranjo unifatorial, com três repetições. Foram determinados índice de acidez, índice de peróxidos, absorção específica, teor de tocoferóis, teor de compostos fenólicos, teor de carotenoides, teor de clorofilas, perfil de ácidos graxos e estabilidade oxidativa. Os azeites provenientes das cultivares Coratina e Frantoio foram classificados como extra virgens. O azeite da cultivar Coratina apresentou maiores teores de pigmentos, seguido pelo da cultivar Koroneiki. A cultivar Coratina ainda apresenta maiores conteúdos de compostos fenólicos (1.725,5 mg kg⁻¹) e de tocoferóis (437,8 mg kg⁻¹). O ácido graxo majoritário em todas as amostras é o oleico.

Termos para indexação: *Olea europaea*, compostos bioativos, ácidos graxos, período de indução, azeitona, parâmetros de qualidade.

Introduction

The consumption of extra-virgin olive oil has increased significantly due to its unique sensory characteristics and health benefits. Typical aroma, flavor, color, and functional properties allow distinguishing olive oil from other edible vegetable oils (Fadda et al., 2012).

Olive oil, as well as other oils and fats, besides contributing to the quality of certain foodstuffs,

provides nutritional value as a good source of metabolic energy, as well as essential linoleic and α -linolenic fatty acids. Its composition is characterized by a high content of a monounsaturated fatty acid, the oleic acid (Krichene et al., 2010), associated with high levels of bioactive compounds such as tocopherols, phenolic compounds, phytosterol (mainly β -sitosterol) and pigments (chlorophylls and carotenoids), which contribute to its sensory characteristics, as well as the

oxidative stability (Allalout et al., 2009; Krichene et al., 2010; Fregapane & Salvador, 2013). Important functions are also assigned to bioactive compounds, such as the participation in the prevention of cardiovascular diseases, cancers, degenerative diseases, and obesity (Fadda et al., 2012; Cicerale et al., 2013). However, olive oil is quite susceptible to lipid oxidation, a spontaneous and unavoidable phenomenon, with direct implication on the commercial value of the oils, either in pure oil or in products containing oil in their formulation, as food, cosmetics, and medicines (Silva et al., 1999).

Scientific interest in olive cultivation in the state of Rio Grande do Sul, Brazil, is due to suitable characteristics for olive oil production, especially from the Coratina, Frantoio, and Koroneiki cultivars, which have shown high and constant fruit productivity (Coutinho et al., 2009; Servili, 2015). Arbequina, one of the most suitable cultivars for olive production, presents good adaptation to Brazilian soil and exhibits vegetative vigor, precocity, and high yielding capacity (Coutinho et al., 2009). Therefore, quality, chemical composition, and stability of oils produced in Southern Brazil should be investigated.

The objective of this work was to characterize the chemical composition of olive oils produced in Southern of Brazil and correlate it with oxidative stability.

Materials and Methods

Experiments were conducted in the chromatography laboratory at Universidade Federal de Pelotas, located in the municipality of Capão do Leão, state of Rio Grande do Sul, Brazil. Olive oil samples were obtained from the Arbequina, Coratina, Frantoio, and Koroneiki cultivars during the 2013/2014 harvest, from adult plants of *Olea europaea* L., from the experimental unit of Embrapa Clima Temperado, located in the municipality of Pelotas, Rio Grande do Sul, Brazil (52°21'W, 31°52'S, at an altitude of 224 m). The soil of the region is classified as Luvissole Hipocrômico órtico típico (Alfisols), a shallow clayey soil (Santos et al., 2006). The climate is characterized as humid with hot summers, according to the Köppen & Geiger classification system (1928) with an annual average temperature of 18.4°C and rainfall of 1,582 mm.

Oil extraction was performed by fruit rupture and centrifugation using the Abencor system, consisting of

a MM-100 mill, a TB 100 thermobeaater, and a CF-100 centrifuge (MC2, Ingeniería y Systemas, Sevilla, Spain) with subsequent decantation and filtration. Samples were packed in amber glasses and kept frozen at -80°C in an ultra freezer (Ilshin Cab, Co., Ltd., Tongjin-eup, South Korea) until the analysis was initiated. The olive fruits used in the oil extraction were obtained from a completely randomized experimental design, in a factorial arrangement, with three replicates.

The reagents and solvents used in the experiment were ethyl ether, ethyl alcohol, potassium hydroxide, acetic acid, sulfuric acid, chloroform, sodium thiosulfate, hexane, methanol, sodium carbonate, Folin-Ciocalteu reagent, phenolphthalein indicator, potassium iodide, and gallic acid of analytical grade; isopropanol, isooctane, methanol, ethanol, and n-hexane (HPLC grade) were purchased from Sigma-Aldrich (São Paulo, Brazil) and Synth (Diadema, Brazil).

The fatty acid methyl ester mix containing caproic, caprylic, caproleic, lauric, dodecenoic, myristic, myristoleic, palmitic, palmitoleic, margaric, stearic, oleic, linoleic, linolenic, arachidic, gadoleic, eicosadienoic, eicosatrienoic, tetraenoic, lignoceric, and nervonic acids were purchased from Sigma Chemicals Co. (St. Louis, USA). The δ and γ -tocopherol standards (90 and \geq 96% purity, respectively) were obtained from Sigma Co. (St. Louis, USA), and α -tocopherol (99% purity) from Merck (Darmstadt, Germany).

The acidity and peroxide value of the samples were determined respectively, according to the America Oil Chemists' Society (AOCS) methods Ca 5a – 40 (Firestone, 1998) and Cd 8-53 (Firestone, 1998). Specific absorption was measured at 232 and 270 nm (K_{232} and K_{270}) according to the method recommended by International Olive Council (IOOC) (2010), and tocopherol content was determined according to the method described by Pestana et al. (2008), with minor modifications. Approximately 0.250 mg olive oil was diluted in isopropanol (high-performance liquid chromatography grade) up to 5 mL and the mixture was centrifuged for 6 min at 9,000 g in a microcentrifuge (NT800 Nova Técnica, Piracicaba, SP, Brazil). The organic phase was transferred to a 1.5-mL vial and samples between 10 to 20 μ L were analysed using the high-performance liquid chromatography system (Shimadzu, Kyoto, Japan),

consisting of the LC-10ATVP solvent mixing module, FCV-10ALVP degasser, DGU-14A reodine pump, SCL-10AVP system control, CTO-10ASVP column oven, and SIL-10AF automatic sampler. Tocopherol separation was performed using the Shimadzu reverse phase analytical column, Shim-Pack CLC-ODS (3.9 cm x 150 mm x 4 μ m), having octadecyl groups as stationary phase, and a fluorescence detector with 290 and 330 nm of excitation and emission wavelength, respectively. Data were acquired and processed using the Class-VP software (Shimadzu, Kyoto, Japan). A mixture of acetonitrile: methanol: isopropanol in the ratio of 50:40:10 (v/v/v) was used as the starting mobile phase for 10 min, changing linearly at 1 mL min⁻¹ constant flow to acetonitrile: methanol: isopropanol 30: 65: 5, (v/v/v) up to 12 min, and returning linearly to the initial mobile phase up to 15 min of analysis.

The identification and quantification of tocopherols were performed using external calibration curves of ($\beta + \gamma$)- and δ -tocopherol, and the results were expressed as milligrams of tocopherol per 100 g of sample.

The extraction of phenolic compounds followed the method described by Montedoro et al. (1992), with modifications. An oil sample of 2.5 g was mixed with 2.0 mL methanol: water (70:30) mixture and 2 mL hexane, subjected to vigorous stirring for 1 min, followed by continuous agitation for 20 min, and centrifugation at 7,000 g at 4°C for 10 min in the 5430R microcentrifuge (Eppendorf Hamburg, Germany). The hydroalcoholic phase was collected and centrifuged again at 7,000 g at 4°C for 4 min, transferred to a 2-mL volumetric flask, and the volume completed with a methanol: water (70:30) mixture. Total phenolic compounds were determined, as described by Gambacorta et al. (2010), by mixing 100 μ L of the hydroalcoholic extract with 100 μ L of the Folin-Ciocalteu reagent at 2 mol L⁻¹ in a falcon tube and, after 4 min, adding 800 μ L 5% sodium carbonate. The mixture was kept in a water bath for 20 min at 40°C. Samples were subjected to absorbance measurements at 750 nm in 6705 UV/VIS spectrophotometer (Jenway, Staffordshire, UK). For total phenolic compound quantification, a gallic acid standard curve was constructed, with readings at 750 nm. The results were expressed as mg kg⁻¹ of gallic acid.

The carotenoid content was determined as described by Rodrigues-Amaya (2001), with readings at 450 nm. The results were expressed as mg kg⁻¹ β -carotene.

Total chlorophyll was determined at 630, 670, and 710 nm using the Cc 13d-55 methodology of AOCS (Firestone, 1998). For both analyses, a blend of iso-octane: ethanol (3:1) was used as a reference, and the results were expressed as mg kg⁻¹. The both readings were performed on 6705 UV/VIS spectrophotometer (Jenway, Staffordshire, UK).

The olive oil samples were derivatized according Hartmann & Lago (1973). Fatty acids were quantified in a gas chromatograph (Perkin Elmer Clarus 500, Shelton, USA), fitted with a FID detector, using a polyethylene glycol ID Carbowax 20M column (0.25 μ m, 30 m x 0.25 mm). The temperature gradient was maintained at 90°C for 1 min, increased at a 12°C min⁻¹ rate up to 160°C for 3.5 min, then increased at a rate of 1.2°C min⁻¹ up to 190°C, with a linear increase of 15°C min⁻¹ up to 230°C for 15 min. The injector and detector temperatures were maintained at 250°C. Nitrogen at a rate of 1.5 mL min⁻¹ was used as carrier gas (Zambiasi, 1997). Fatty acid methyl esters were identified by comparison with retention times of reference standards, and results were expressed as relative fatty acid percentage.

Oxidative stability was determined in the oil samples in the 743 Rancimat (Metrohm, Herisau, Switzerland) at 110°C, at an inflation rate of 10 L h⁻¹, according to EN ISO14112 (CEN, 2003).

Data were analyzed for normality by the Shapiro-Wilk test, homoscedasticity by the Hartley test, and residue independence by the graphic analysis. Subsequently, data were subjected to the analysis of variance through the F-test, at 5% probability. The effects of cultivars were compared by Tukey's test, at 5% probability, and correlations between dependent variables were analyzed using Pearson's correlation coefficient (SAS Institute Inc., Cary, NC).

Results and Discussion

Differences were observed in acidity values, except for the oils from the Coratina and Koroneiki cultivars (Table 1). In addition, only the oil from the Arbequina cultivar was not in line with the established legislation standards for extra-virgin olive oil (0.8%), and it was classified as lampante virgin olive oil because it features acidity higher than 2% (Brasil, 2012).

Several factors can lead to high acidity content, including harvesting process, fruit maturation index,

olive quality, storage, and oil extraction. According to Cardoso et al. (2010), storage and oil extraction should not exceed 4 hours. The authors found high acidity content at the end of harvest, with values of 2.2 and 3.6%, respectively, in the Ascolano and Negrao cultivars. The high acidity may have been due to the injury in fruits and time of exposure of the olives at room temperature, favoring enzyme activity, and increasing acidity values.

Peroxide values of olive oils from the Coratina and Frantoio cultivars were within the limits allowed for the classification of extra-virgin olive oil, according to Brasil (2012) and IOOC (2012). The other samples presented values above the limits established for extra-virgin and virgin olive oils. These results were probably due to the longer exposure time of the fruits before oil extraction or the greater injury between harvest and processing. Cardoso et al. (2010) also found high peroxide values in the oil from the Negrao olive cultivar (25.5%), similar to the one found in oil from the Koroneiki cultivar.

Oils from the Coratina and Frantoio cultivars presented specific absorption coefficients (K_{270}) in accordance with the extra-virgin oil classification

(Table 1). For the other samples, the specific absorption coefficients K_{232} were within the limit for classification of extra-virgin olive oil. As the process of obtaining the oil was the same for all cultivars, it is assumed that differences in this parameter may be related to the characteristics of each cultivar. Dabbou et al. (2010) reported similar results to those obtained in this study for the oils from the Arbequina and Koroneiki cultivars.

Oil from the Coratina cultivar stood out due to the highest tocopherol content, with α -tocopherol as the major compound in all oils (Table 2). Separation of γ and β -tocopherol was not possible by the reverse phase column (Figure 1), so that results were expressed as the sum of both compounds.

Oils of the Arbequina and Frantoio cultivars presented lower tocopherol content, which varies according to the cultivar (Table 2). It should be noted that this compound plays an important role in the olive oil stability (Allouche et al., 2007). This variation is confirmed in the literature, with reports of α -tocopherol content in virgin olive oil between 100 and 460 mg kg⁻¹, representing 96% of total tocopherols

Table 1. Mean±standard deviation of quality indexes of olive (*Olea europaea*) oils from Arbequina, Coratina, Frantoio, and Koroneiki cultivars⁽¹⁾.

Cultivar	Free acidity (g 100g ⁻¹ oleic acid)	Peroxide (meq g kg ⁻¹ O ₂)	K_{232} (nm)	K_{270} (nm)
Arbequina	2.22±0.01a	36.23±1.14a	2.70±0.01a	0.22±0.02a
Coratina	0.49±0.01c	11.20±1.20c	1.71±0.03d	0.15±0.02b
Frantoio	0.79±0.03b	13.91±1.18c	2.03±0.01b	0.14±0.01b
Koroneiki	0.55±0.05c	21.60±1.17b	1.88±0.10c	0.22±0.01a
Coefficient of variation (%)	3.0	5.6	2.5	6.7

⁽¹⁾Means followed by equal letters, in the column, do not differ by Tukey's test, at 5% probability. K_{232} and K_{270} , specific absorption measured at 232 and 270 nm, respectively. n=3.

Table 2. Mean±standard deviation of bioactive compounds of olive (*Olea europaea*) oils from Arbequina, Coratina, Frantoio, and Koroneiki cultivars⁽¹⁾.

Cultivar	β + γ -tocopherol (mg kg ⁻¹)	α -tocopherol (mg kg ⁻¹)	δ -tocopherol (mg kg ⁻¹)	Phenolic compounds (mg kg ⁻¹ gallic acid)	Carotenoids (mg kg ⁻¹ β -carotene)	Chlorophyll (mg kg ⁻¹)
Arbequina	7.50±0.01d	219.98±8.84c	4.10±0.13b	651.74±6.90b	3.97±0.01c	0.84±0.02c
Coratina	22.52±0.41a	410.31±6.27a	5.01±0.03a	1,725.53±4.27a	9.39±0.06a	1.94±0.01a
Frantoio	8.92±0.12c	181.77±3.47d	1.98±0.05c	468.06±2.91c	3.93±0.04c	0.53±0.02d
Koroneiki	10.93±0.29b	285.64±3.62b	1.85±0.05c	437.18±3.19d	4.75±0.02b	0.90±0.01b
CV (%)	2.1	2.2	2.4	0.6	0.7	1.6

⁽¹⁾Means followed by equal letters, in the column, do not differ by Tukey's test, at 5% probability. CV, coefficient of variation. n=3.

content (Allouche et al., 2007; Gambacorta et al., 2010; Mansouri et al., 2014).

Regarding phenolic compound content, olive oil from the Coratina cultivar presented higher values than those of the other samples. Possibly the cultivar, fruit maturation index, and storage at ambient or refrigerated temperatures were responsible for the different levels observed in this study. Phenolic compounds also contribute to the peculiar aroma and flavor of olive oil, which are believed to significantly enhance oxidative stability due to their antioxidant properties (Allouche et al., 2007).

The oil from the Coratina cultivar stood out from the others due to this higher pigment content. Confirming this result, Aparicio-Ruiz et al. (2009) reported the β -carotene levels for the oils from the Coratina (4.04 and 5.41 mg kg⁻¹), Frantoio (4.03 and 4.80 mg kg⁻¹), and

Koroneiki (3.89 and 6.26 mg kg⁻¹) cultivars close to those found in the olive cultivars from Southern Brazil.

Chlorophylls act as pro-oxidants in the presence of light; thus, variations in their oil contents, together with inadequate storage conditions, may affect the shelf life of the product (Bengana et al., 2013). According to the literature, the centrifugation process, which was used to obtain the Brazilian olive oils, produces high losses of pigments in relation to the pressing process used in other countries (Torres & Maestri, 2006). This may explain in part the lower content of pigments found in Brazilian olive oils.

As expected, it was verified that the major fatty acids were oleic, palmitic, and linoleic (Table 3). The oleic fatty acid was the most representative in all samples, with higher content in olive oil from the Koroneiki cultivar (76.5 %) and lower content in olive oil from

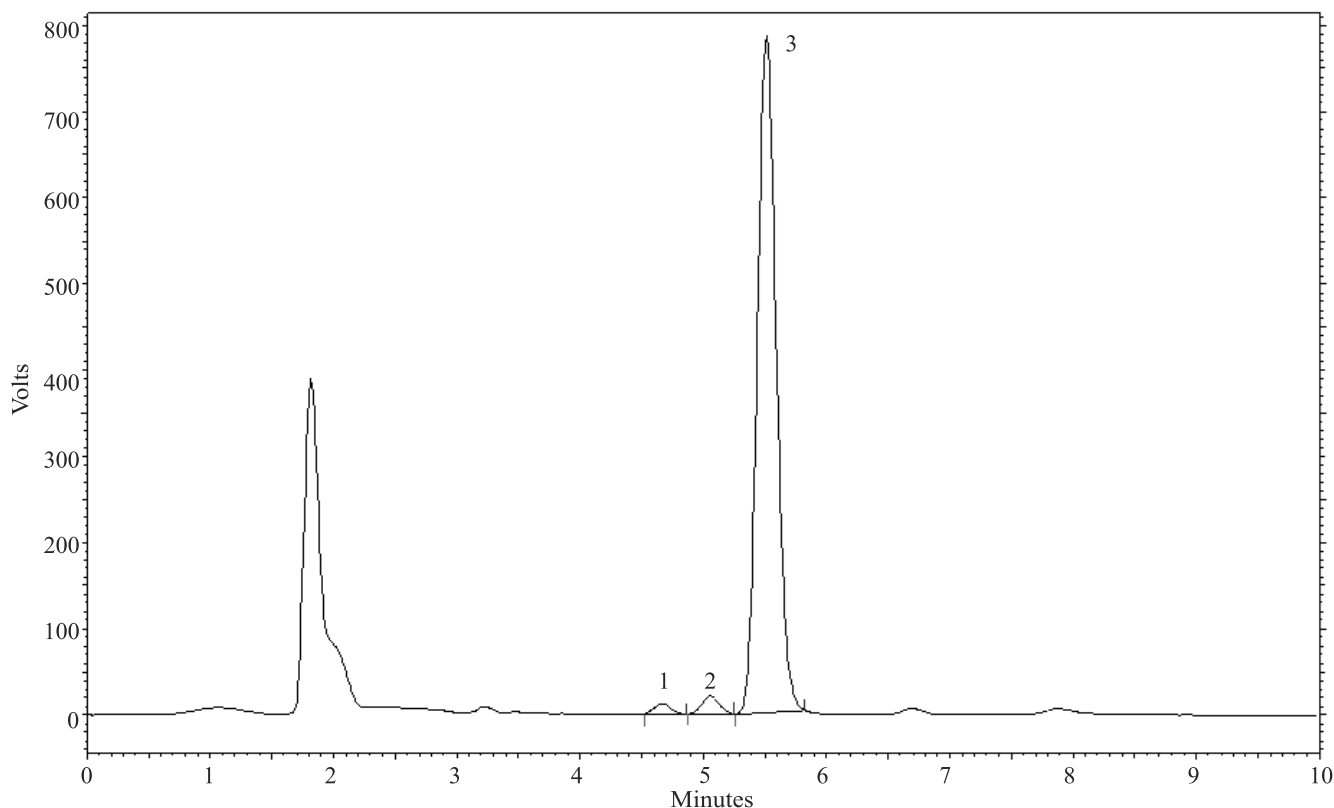


Figure 1. Typical chromatogram of δ -, β + γ -, and α -tocopherols separation of olive (*Olea europaea*) oil from the Arbequina cultivar by high-performance liquid chromatography using reverse phase RP-18CLS-ODS column and fluorescence detector, excitation at 290 nm, and emission at 330 nm. The peaks correspond to: 1, δ -tocopherol; 2, β + γ -tocopherol, and 3, α -tocopherol.

Arbequina (59.2%). These results are in alignment with the values recommended by the Brazilian legislation (Brasil, 2012; IOOC, 2012). Dabbou et al. (2010) reported, respectively, 61.4 and 76.0% for oleic acid in olive oil from the Arbequina and Koroneiki cultivars grown in Southern Tunisia. Daskalaki et al. (2009) found values from 75.1 to 78.5% for olive oil from the Koroneiki cultivar produced in Greece. Therefore, depending on the cultivar and the origin region, the relative percentage of the fatty acids varies.

Although the Arbequina cultivar is easily adaptable to the Brazilian soil and is well indicated for olive oil production, it is disadvantageous because it provides a oil with lower levels of oleic acid, which partially contributes to its lower stability (Mello & Pinheiro, 2012). In the present study, the oil of this cultivar showed the highest content of saturated fatty acid; the palmitic acid content was the highest (18.5%), close to the maximum value of 20% established by Brasil (2012) and IOOC (2012) (Figure 2).

The oils from the Frantoio and Arbequina cultivars stood out for total linoleic acid content, adding up to 14.8 and 16.6%, respectively. However, it is known that oil stability to lipid oxidation is directly correlated with the number of double bonds present in the chain, which are susceptible to oxidation (Yun & Surh, 2012). Furthermore, the essential compound group represented by omega-6 fatty acids, precursor for arachidonic acid (C 20:4), and omega-3 fatty acids, precursor for both eicosapentaenoic acid EPA (C 20:5), and docosahexaenoic DHA (C 22:6) are related to the

prevention of cardiovascular diseases, contributing to the metabolism regulation of low-density lipoprotein (LDL) (Dolinsky, 2009).

In addition to the palmitic, palmitoleic, stearic, oleic, linoleic, and linolenic fatty acids (Table 3), the following fatty acids were also observed, but in small amounts (<0.5%): myristic (C 14:0), margaric (C 17:0), margaroleic (C 17:1), arachidic (C 20:0), gadoneic (C 20:1), behenic (C 22:0), and lignoceric (C 24:0). The fatty acid content found in the present study are in alignment with those recommended by Brasil (2012) and IOOC (2012).

Differences in oxidative stability were verified between samples, and greater stability was observed for the olive oil from the Coratina cultivar (Table 3). Lower peroxide, acidity, and polyunsaturated fatty acid ratio, as well as higher contents of bioactive compounds, may have positively affected the oxidative stability of this olive oil.

These results corroborate those presented by Ramalho & Jorge (2006), who evaluated the oxidative stability of soy oil by Rancimat at 110°C. By adding the antioxidants α -tocopherol and rosemary extract to the oils, the authors demonstrated their protective effect on oxidation. Oils with higher oxidative stability also showed higher α -tocopherol contents.

A high positive correlation coefficient ($r = 0.99$, $p < 0.0001$) was observed for carotenoids and ($\gamma + \beta$)-tocopherol contents, confirming that an increase in carotenoids can lead to an increase in ($\gamma + \beta$)-tocopherol (Table 4). Positive correlations were also

Table 3. Mean and standard deviations (SD) of main fatty acids and oxidative stability of olive (*Olea europaea*) oils from Arbequina, Coratina, Frantoio, and Koroneiki cultivars⁽¹⁾.

Cultivar	C 16:0	C 16:1	C 18:0	C 18:1	C 18:2	C 18:3	C 20:0	C 20:1	C 24:0	Total saturated	Total unsaturated	Oxidative stability (h)
	------(%)-----											
Arbequina	18.51a	3.34a	1.20b	59.15d	15.79a	0.76c	0.39b	0.27b	0.18b	20.51a	79.49c	3.22d
SD	0.15	0.10	0.03	0.10	0.07	0.03	0.02	0.00	0.00	0.20	0.20	0.06
Coratina	14.19c	0.58c	1.66b	72.11b	9.19c	1.00a	0.39b	0.32a	0.21a	16.36c	83.64a	20.47a
SD	0.06	0.00	0.06	0.29	0.24	0.00	0.02	0.02	0.00	0.01	0.01	0.24
Frantoio	15.12b	1.34b	1.59b	66.11c	13.94b	0.85b	0.32c	0.31a	0.10d	17.21b	82.79b	5.64c
SD	0.01	0.01	0.02	0.01	0.01	0.03	0.00	0.00	0.00	0.03	0.03	0.15
Koroneiki	12.82d	0.75c	2.49a	76.47a	5.52d	0.75c	0.46a	0.32a	0.13c	16.07c	83.93a	11.81b
SD	0.06	0.00	0.23	0.11	0.03	0.00	0.00	0.00	0.00	0.16	0.16	0.06
CV (%)	0.6	3.3	6.8	0.2	1.1	2.7	3.9	3.8	4.5	0.7	0.1	1.4

⁽¹⁾Means followed by equal letters, in the column, do not differ by Tukey's test, at 5% probability. CV, coefficient of variation mean of three replicates.

Table 4. Pearson correlation coefficients and p-value among the dependent variables of olive (*Olea europaea*) oils from the Arbequina, Coratina, Frantoio, and Koroneiki cultivars⁽¹⁾.

Variable	AC (1)	PV (2)	K ₂₃₂ (3)	K ₂₇₀ (4)	GTOC (5)	ATOC (6)	DTOC (7)	TP (8)	TC (9)	TCL (10)	C 16 (11)	C 18 (12)	C 18:1 (13)	C 18:2 (14)	C 18:3 (15)	TS (16)	TU (17)	RAN (18)
(1)	1.000	0.900*	0.981	0.474	-0.583	-0.496	0.268	-0.283	-0.499	-0.356	0.958	-0.508	-0.887	0.774	-0.485	0.969	-0.969	0.089
(2)		1.000	0.898	0.788	-0.646	-0.442	0.400	0.372	0.098	0.256	0.0002	0.198	0.003	0.024	0.223	<0.001	<0.001	0.835
(3)			1.000	0.482	-0.704	-0.619	0.811	0.148	-0.574	-0.400	0.729	-0.083	-0.606	0.444	-0.753	0.765	-0.765	0.519
(4)				1.000	0.112	0.032	0.736	0.164	0.028	0.198	0.040	0.845	0.111	0.271	0.031	0.027	0.027	0.187
(5)					1.000	0.658	0.700	0.156	-0.629	-0.499	0.942	-0.497	-0.897	0.798	-0.562	0.961	-0.961	0.123
(6)						1.000	0.623	0.938	0.028	0.099	0.0005	0.210	0.002	0.018	0.147	0.0001	0.0001	0.772
(7)							1.000	0.845	-0.412	-0.251	0.213	0.442	-0.023	-0.169	-0.714	0.244	-0.244	0.825
(8)								1.000	0.183	0.431	0.613	0.273	0.957	0.690	0.047	0.560	0.560	0.012
(9)									0.994	0.955	-0.462	-0.002	0.514	-0.470	0.888	-0.541	0.541	-0.485
(10)									<0.001	<0.001	0.249	0.997	0.193	0.240	0.003	0.166	0.166	0.224
(11)									<0.001	<0.001	-0.448	0.162	0.570	-0.589	0.715	-0.524	0.524	-0.221
(12)									0.952	0.967	0.266	0.701	0.140	0.125	0.047	0.182	0.182	0.599
(13)									<0.001	<0.001	0.774	0.461	0.656	0.701	0.002	0.608	0.608	0.092
(14)									1.000	0.978	-0.373	-0.065	0.441	-0.410	0.888	-0.458	0.458	-0.498
(15)									<0.001	<0.001	0.362	0.878	0.275	0.313	0.003	0.254	0.254	0.209
(16)									1.000	1.000	-0.266	-0.059	0.379	-0.390	0.806	-0.351	0.351	-0.398
(17)									<0.001	<0.001	0.524	0.890	0.354	0.340	0.016	0.394	0.394	0.329
(18)									1.000	1.000	1.000	-0.730	-0.969	0.901	-0.259	0.992	-0.992	-0.195
									0.040	<0.001	0.040	0.040	<0.001	0.002	0.536	<0.001	<0.001	0.643
									1.000	0.800	1.000	1.000	0.800	-0.860	-0.354	-0.668	0.668	0.782
									0.017	0.017	0.006	0.017	0.006	0.390	0.070	0.070	0.070	0.022
									1.000	1.000	<0.001	1.000	1.000	<0.001	0.590	<0.001	<0.001	0.313
											1.000	1.000	1.000	1.000	-0.122	0.894	-0.894	-0.452
															0.774	0.003	0.003	0.261
															1.000	-0.340	0.340	-0.798
															0.410	0.410	0.410	0.018
															1.000	1.000	-1.000	-0.124
															<0.001	<0.001	<0.001	0.770
															1.000	1.000	1.000	0.124
															0.770	0.770	0.770	0.770
															1.000	1.000	1.000	1.000

⁽¹⁾AC, free acidity; PV, peroxide value; K₂₃₂ and K₂₇₀, specific absorption measured at 232 and 270 nm, respectively; GTOC, γ + β -T; gamma + beta-tocopherol; ATOC, α -T; alpha-tocopherol; DTOC, δ -T; delta-tocopherol; TP, total phenolics; TC, total carotenoids; TCL, total chlorophylls; fatty acids: C 16:0, palmitic; C 18:0, stearic; C 18:1, oleic; C 18:2, linoleic; C 18:3, linolenic; TS, total saturated fat; TU, total unsaturated fat; RAN, oxidative stability in Rancimat. *Pearson's correlation coefficients. **p-value.

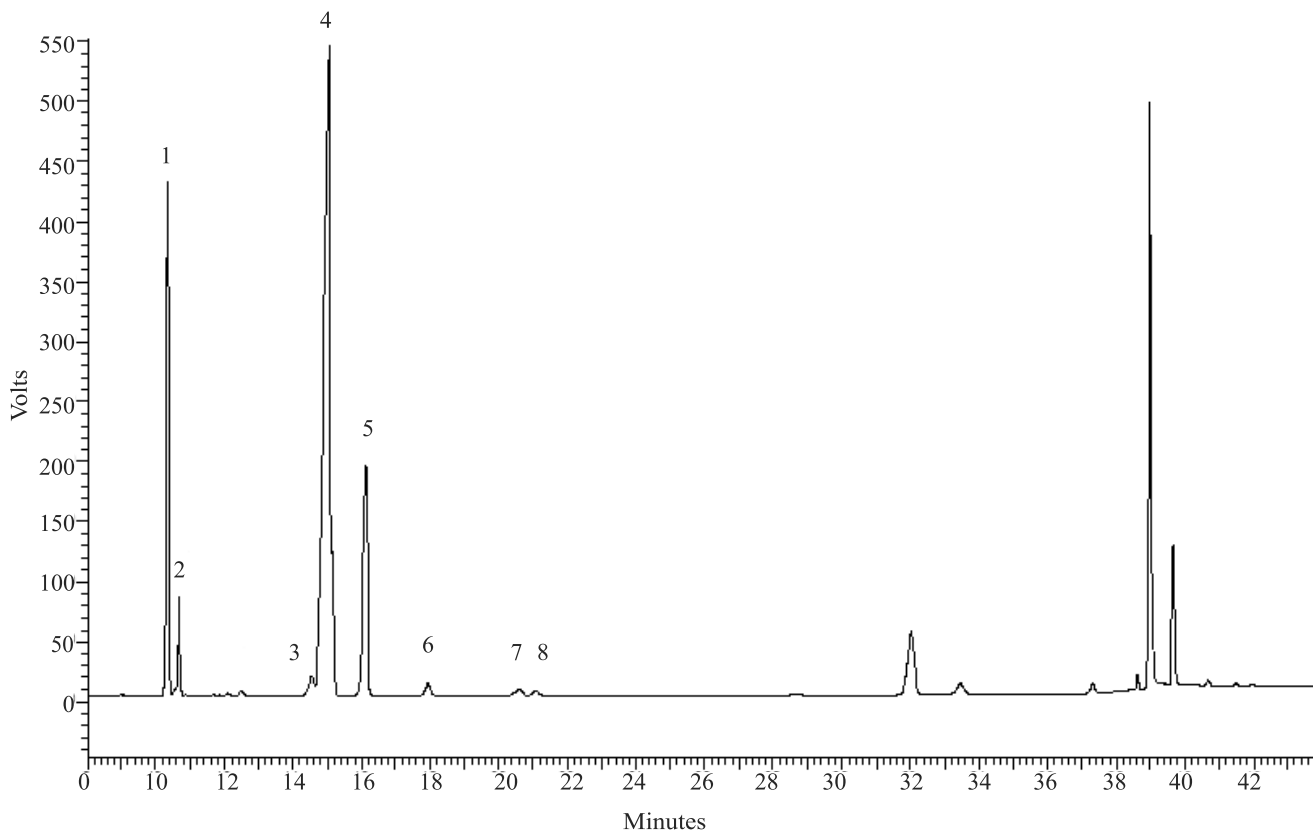


Figure 2. Typical chromatogram of fatty acid separation of olive (*Olea europaea*) oil from the Arbequina cultivar, using a gas chromatograph, equipped with a FID detector. The peaks correspond to the fatty acids: 1, palmitic; 2, palmitoleic; 3, stearic; 4, oleic; 5, linoleic; 6, linolenic; 7, arachidic; and 8, gadoleic.

observed between the phenolic compounds and tocopherols ($\gamma + \beta$)-tocopherol; and α -tocopherol and δ -tocopherol. A high positive correlation was found between chlorophyll content and ($\gamma + \beta$)-tocopherol; and α -tocopherol and δ -tocopherol.

The phenolic compounds, carotenoids, tocopherol, and fatty acid profiles contributed positively to oil stability. Olive oil from the Coratina cultivar presented higher contents of bioactive compounds and, consequently, greater oxidative stability. However, the oxidation reaction occurs through several mechanisms, which makes its elucidation very complex.

The production of olive oil in Brazil is still small, but of great importance for a boost in the country's olive crop. Thus, this study provides data on oils obtained from the most expressive cultivars in the southern region of Rio Grande do Sul, Brazil. In this

scenario, many possibilities open up, and there is great motivation for further investigative research.

Conclusions

1. The olive (*Olea europaea*) oils from the Coratina and Frantoio cultivars produced in Southern Brazil are classified as extra-virgin, in alignment with the quality parameters established for the product.

2. Olive oil from the Coratina cultivar presents greater oxidative stability due to a higher content of phenolic compounds, carotenoids, and tocopherols.

Acknowledgments

To Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes) and to Fundação de Amparo à Pesquisa do Estado do Rio Grande do Sul (Fapergs), for financial support.

References

- ALLALOUT, A.; KRICHENÉ, D.; METHENNI, K.; TAAMALLI, A.; OUESLATI, I.; DAOUD, D.; ZARROUK, M. Characterization of virgin olive oil from super intensive spanish and greek varieties grown in northern Tunisia. **Scientia Horticulturae**, v.120, p.77-83, 2009. DOI: 10.1016/j.scienta.2008.10.006.
- ALLOUCHE, Y.; JIMÉNEZ, A.; GAFORIO, J.J.; UCEDA, M.; BELTRÁN, G. How heating affects extra virgin olive oil quality indexes and chemical composition. **Journal of Agricultural and Food Chemistry**, v.55, p.9646-9654, 2007. DOI: 10.1021/jf070628u.
- APARÍCIO-RUIZ, R.; GANDUL-ROJAS, B.; ROCA, M. Pigment profile in non-spanish olive varieties (*Olea europae* L. var. Coratina, Frantoio and Koroneiki. **Journal of Agricultural and Food Chemistry**, v.57, p.10831-10836, 2009. DOI: 10.1021/jf9027393.
- BENGANA, M.; BAKHOUCHE, A.; LOZANO-SÁNCHEZ, J.; AMIR, Y.; YOUYOU, A.; SEGURA-CARRETERO, A.; FERNÁNDEZ-GUTIÉRREZ, A. Influence of olive ripeness on chemical properties and phenolic composition of Chemlal extra-virgin olive oil. **Food Research International**, v.54, p.1868-1875, 2013. DOI: 10.1016/j.foodres.2013.08.037.
- BRASIL. Ministério da Agricultura, Pecuária e Abastecimento. Instrução Normativa nº 1, de 30 de janeiro de 2012. [Estabelece o Regulamento Técnico do Azeite de Oliva e do Óleo de Bagaço de Oliva e os limites de tolerância]. **Diário Oficial da União**, 1 fev. 2012. Seção 1, p.5-8. Available at: <<http://pesquisa.in.gov.br/imprensa/jsp/visualiza/index.jsp?data=01/02/2012&jornal=1&pagina=5&totalArquivos=112>>. Accessed on: Oct. 3 2017.
- CARDOSO, L.G.V.; BARCELOS, M. de F.P.; OLIVEIRA, A.F. de; PEREIRA, J. de A.R.; ABREU, W.C. de; PIMENTEL, F. de A.; CARDOSO, M. das G.; PEREIRA, M.C. de A. Características físico-químicas e perfil de ácidos graxos de azeites obtidos de diferentes variedades de oliveiras introduzidas no Sul de Minas Gerais – Brasil. **Semina: Ciências Agrárias**, v.31, p.127-136, 2010.
- CEN. European Committee for Standardization. **EN 14112:2003**: Fat and Oil Derivatives: Fatty Acid Methyl Esters (FAME): determination of oxidative stability (accelerated oxidation test). Brussels, 2003.
- CICERALE, S.; CONLAN, X.A.; BARNETT, N.W.; KEAST, R.S.J. Storage of extra virgin olive oil and its effect on the biological activity and concentration of oleocanthal. **Food Research International**, v.50, p.597-602, 2013. DOI: 10.1016/j.foodres.2011.03.046.
- COUTINHO, E.F.; RIBEIRO, F.C.; CAPPELLARO, T.H. (Ed.). **Cultivo de oliveira (*Olea europaea* L.)**. Pelotas: Embrapa Clima Temperado, 2009. 126p. (Embrapa Clima Temperado. Sistema de produção, 16).
- DABBOU, S.; BRAHMI, F.; TAAMALI, A.; ISSAOUI, M.; OUNI, Y.; BRAHAM, M.; ZARROUK, M.; HAMMAMI, M. Extra virgin olive oil components and oxidative stability from olives grow in Tunisia. **Journal of the American Oil Chemists Society**, v.87, p.1199-1209, 2010. DOI: 10.1007/s11746-010-1600-3.
- DASKALAKI, D.; KEFI, G.; KOTSIU, K.; TASIOULA-MARGARI, M. Evaluation of phenolic compounds degradation in virgin olive oil during storage and heating. **Journal of Food and Nutrition Research**, v.48, p.31-41, 2009.
- DOLINSKY, M. (Org.). **Nutrição funcional**. São Paulo: Roca, 2009. 204p.
- FADDA, C.; DEL CARO, A.; SANGUINETTI, A.M.; URGEGHE, P.P.; VACCA, V.; ARCA, P.P.; PIGA, A. Changes during storage of quality parameters and in vitro antioxidant activity of extra virgin monovarietal oils obtained with two extraction technologies. **Food Chemistry**, v.134, p.1542-1548, 2012. DOI: 10.1016/j.foodchem.2012.03.076.
- FIRESTONE, D. (Ed.). **Official Methods and Recommended Practices of the American Oil Chemists Society**. 5th ed. Champaign: AOCS, 1998. 2v.
- FREGAPANE, G.; SALVADOR, M.D. Production of superior quality extra virgin olive oil modulating the content and profile of its minor components. **Food Research International**, v.54, p.1.907-1914, 2013. DOI: 10.1016/j.foodres.2013.04.022.
- GAMBACORTA, G.; FACCIA, M.; PREVITALI, M.A.; PATI, S.; LA NOTTE, E.; BAIANO, A. Effects of olive maturation and stoning on quality indices and antioxidant Content of extra virgin oils (cv. *Coratina*) during Storage. **Journal of Food Science**, v.75, p.229-235, 2010. DOI: 10.1111/j.1750-3841.2010.01516.x.
- HARTMAN, L.; LAGO, R.C.A. Rapid preparation of fatty acid methyl esters from lipids. **Laboratory Practice**, v.22, p.475-477, 1973.
- IOOC. International Olive Oil Council. **Method of analysis**: spectrophotometric investigation in the ultraviolet. Madri, 2010. 11p. COI/T20/Doc. no. 19/Rev. 3.
- IOOC. International Olive Oil Council. **Trade standard applying to olive oils and olive-pomace oils**. Madri, 2012. 16p. COI/T.15/NC No 3/Rev. 7.
- KÖPPEN, W.; GEIGER, R. **Klimate der Erde**. Gotha: Verlag Justus Perthes, 1928. Wall-map, 150 x 200 cm.
- KRICHE, D.; ALLALOUT, A.; MANCEBO-CAMPOS, V.; SALVADOR, M.D.; ZARROUK, M.; FREGAPANE, G. Stability of virgin olive oil and behaviour of its natural antioxidants under medium temperature accelerated storage conditions. **Food Chemistry**, v.121, p.171-177, 2010. DOI: 10.1016/j.foodchem.2009.12.026.
- MANSOURI, F.; BEN MOUMEN, A.; HOUMY, N.; RICHARD, G.; FAUCONNIER, M.L.; SINDI, M.; SERGHINI-CAID, H.; ELAMRANI, A. Evaluación de la estabilidad oxidativa de los aceites de oliva obtenidos a partir de la mezcla de aceite “Arbequina” con otros aceites de oliva monovarietales. **OLIVAE**, n.120, p.23-30, 2014.
- MELLO, L.D.; PINHEIRO, M.F. Aspectos físico-químicos de azeites de oliva e de folhas de oliveira provenientes de cultivares do RS, Brasil. **Alimentos e Nutrição**, v.23, p.537-548, 2012.
- MONTEDORO, G.; SERVILI, M.; BALDIOLI, M.; MINIATI, E. Simple and hydrolyzable phenolic compounds in virgin olive oil. 1. Their extraction, separation, and quantitative and

- semiquantitative evaluation by HPLC. **Journal of Agricultural and Food Chemistry**, v.40, p.1571-1576, 1992. DOI: 10.1021/jf00021a019.
- PESTANA, V.R.; ZAMBIAZI, R.C.; MENDONÇA, C.R.B.; BRUSCATTO, M.H.; LERMA-GARCÍA, M.J.; RAMIS-RAMOS, G. Quality changes and Tocopherols and γ -Orizanol concentrations in rice bran oil during the refining process. **Journal of the American Oil Chemists' Society**, v.85, p.1013-1019, 2008. DOI: 10.1007/s11746-008-1300-4.
- RAMALHO, V.C.; JORGE, N. Atividade antioxidante do α -tocoferol e do extrato de alecrim em óleo de soja purificado. **Revista do Instituto Adolfo Lutz**, v.65, p.15-20, 2006.
- RODRIGUES-AMAYA, D.B. **A guide to carotenoid analysis in foods**. Washington: ILSI, 2001. 64p.
- SANTOS, H.G. dos; JACOMINE, P.K.T.; ANJOS, L.H.C. dos; OLIVEIRA, V.A. de; OLIVEIRA, J.B. de; COELHO, M.R.; LUMBRERAS, J.F.; CUNHA, T.J.F. (Ed). **Sistema brasileiro de classificação de solos**. 2.ed. Rio de Janeiro: Embrapa Solos, 2006. 412p.
- SERVILI, M. **Her majesty the coratina olive**. Available at: <<http://www.oliofficina.net/knowledge/oil/her-majesty-the-coratina-olive.htm>>. Accessed on: Feb. 15 2015.
- SILVA, F.A.M.; BORGES, M.F.M.; FERREIRA, M.A. Métodos para avaliação do grau de oxidação lipídica e capacidade antioxidante. **Química Nova**, v.22, p.94-103, 1999. DOI: 10.1590/S0100-40421999000100016.
- TORRES, M.M.; MAESTRI, D.M. Chemical composition of arbequina virgin olive oil in relation to extraction and storage conditions. **Journal of the Science of Food and Agriculture**, v.86, p.2311-2317, 2006. DOI: 10.1002/jsfa.2614.
- YUN, J.-M.; SURH, J.H. Fatty acid composition as a predictor for the oxidation stability of Korean vegetable oils with or without induced oxidative stress. **Preventive Nutrition and Food Science**, v.17, p.158-165, 2012. DOI: 10.3746/pnf.2012.17.2.158.
- ZAMBIAZI, R.Z. **The role of endogenous lipid components on vegetable oil stability**. 1997. 304p. Thesis (Doctor) - University of Manitoba, Winnipeg.

Received on February 22, 2016 and accepted on May 15, 2017