

Evaluation of the lipidic composition and antioxidant activity of the seed oil from grapes 'Isabel' and 'Rose Niagara'

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### Abstract

The growth of the wine sector induces an increase in the amounts of waste produced; an alternative to reuse this waste is the extraction of grapeseed oil, which can be used in several applications due to the aroma and antioxidant properties of this oil. This work aimed to evaluate the yield, chemical composition, and antioxidant activity of the seed oil from grapes of the varieties 'Isabel' and 'Rose Niagara'. The oil was extracted using a Soxhlet extractor and hexane as solvent. The oils have had their chemical composition evaluated regarding the presence of fatty acids, which were identified by gas chromatography. The antioxidant capacity of the oils was evaluated by ABTS<sup>+</sup> radical scanning. The treatments were the two grape varieties, with five replicates for each treatment. The data underwent analysis of variance and the means were compared by Tukey's multiple range test at 5% probability. The obtained results of the seed oils showed a statistical difference between varieties. The 'Isabel' variety presented a lower oil (19.12 wt.%), content having stearic acid as the major compound, with 72.08 wt.%. Regarding antioxidant activity, the 'Isabel' variety presented itself superior, with a percentage of ABTS<sup>+</sup> radical scavenging of 22.11%, whereas the 'Rose Niagara' variety presented 20.85%. The seeds of 'Rose Niagara' grapes may be employed as a source of oil due to the higher yield and similar antioxidant activity to the seed oil of 'Isabel' grapes.

Keywords: fatty acids; Vitis sp.; viticulture; antioxidant activity.

#### Resumo

### Avaliação da composição lipídica e da atividade antioxidante do óleo de semente de uvas 'Isabel' e 'Niágara Rosada'

O crescimento do setor vitivinícola leva a um aumento do volume dos resíduos gerados; uma alternativa para reaproveitar estes resíduos é a extração do óleo da semente de uva, que pode ser empregado em diversas áreas, visto que as sementes apresentam propriedades antioxidantes e aromáticas. O objetivo deste trabalho foi avaliar o rendimento, a composição química e a atividade antioxidante do óleo da semente de uva das variedades 'Isabel' e 'Niágara Rosada'. O óleo foi extraído utilizando um extrator Soxhlet com hexano como solvente. O óleo teve sua composição química avaliada quanto à presença de ácidos graxos, que foram identificados por cromatografia gasosa. A capacidade antioxidante foi avaliada através da varredura do radical ABTS<sup>+</sup>. Os tratamentos foram as duas variedades de uva, com cinco repetições por tratamento. Os dados de rendimento e de capacidade antioxidante foram submetidos a ANOVA e teste de Tukey a 5% de probabilidade. Os resultados



obtidos indicaram diferenças entre as variedades. A variedade 'Isabel' apresentou menor rendimento de óleo (19,12% m/m), tendo como principal componente o ácido esteárico, com 42,51% m/m, enquanto que a variedade 'Niágara Rosada' (rendimento de 23,15% m/m) apresentou o ácido oleico como o principal componente, com 72,08% m/m. Em relação à atividade antioxidante, a variedade 'Isabel' apresentou-se superior, com porcentagem de varredura de 22,11% do radical ABTS, enquanto que a variedade 'Niágara Rosada' apresentou 20,85%. As sementes de uvas 'Niágara Rosada' podem ser utilizadas como fonte de óleo devido ao maior rendimento e atividade antioxidante semelhante ao óleo de semente de uvas 'Isabel'.

Palavras-chave: ácidos graxos; Vitis sp.; viticultura; atividade antioxidante.

### Resumen

### Evaluación de la composición lipídica y actividad antioxidante del aceite de semilla de uva 'Isabella' y 'Niágara Rosada'

El crecimiento del sector vitivinícola conlleva un aumento del volumen de residuos generados; una alternativa para reutilizar estos residuos es extraer el aceite de la semilla de uva, que puede ser utilizado en la industria alimentaria, farmacéutica y cosmética, ya que las semillas tienen propiedades antioxidantes y aromáticas. Este trabajo tuvo como objetivo evaluar el rendimiento, la composición química y la actividad antioxidante del aceite de semilla de uvas de las variedades 'Isabella' y 'Niágara Rosada'. El aceite se extrajo usando un extractor Soxhlet y hexano como disolvente. Los aceites han tenido su composición química evaluada en cuanto a la presencia de ácidos grasos por cromatografía de gases. También se evaluó la capacidad antioxidante de los aceites extraídos por medio de barrido de radical ABTS. Los tratamientos fueron las dos variedades de uva, con cinco repeticiones por tratamiento. Los datos se sometieron a ANOVA y prueba de rango múltiple de Tukey con una probabilidad del 5%. Los resultados obtenidos mostraron diferencias estadísticas entre las variedades. La uva "Isabella" presentó un contenido de aceite más bajo, con ácido esteárico como componente principal (42.51% en peso); mientras que la 'Niágara Rosada' tenía ácido oleico como compuesto principal (72.08% en peso). En cuanto a la actividad antioxidante, la variedad 'Isabella' presentó un porcentaje de barrido radical ABTS + del 22.11%, mientras que la variedad 'Niágara Rosada' presentó el 20.85%. Las semillas de las uvas 'Niágara Rosada' se pueden utilizar como fuente de aceite debido al mayor rendimiento y la actividad antioxidante similar al aceite de semilla de las uvas 'Isabella'.

Palabras clave: ácidos grasos; Vitis sp.; viticultura; actividad antioxidante.

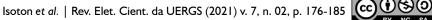
## Introduction

In Brazil, viticulture occupies an area of 74,826 ha and presents a very high plant diversity, with more than 120 cultivars of *Vitis vinifera* L. and more than 40 cultivars of *Vitis labrusca* L. being cultivated in the region, besides the hybrid types (IBGE, 2020; CAMARGO et al., 2011). In the 2019/2020 harvest, it was produced 735,536 t of grapes in Rio Grande do Sul state, South Brazil (IBGE, 2020).

The subtropical climate of the Serra Gaúcha region (Köppen classification Cfa) is characterized by a yearly cycle in which the wines undergo a dormancy/hibernation period that is triggered by the low temperatures in winter (ALVARES *et al.*, 2013). The viticulture with these characteristics occurs in South Brazil (Rio Grande do Sul, Santa Catarina, and Paraná states), and also high-altitude regions in Southeast Brazil, which are colder, such as the eastern part of São Paulo state (CAMARGO *et al.*, 2011).

According to Mello and Machado (2020) and Silva et al. (2020), Brazilian grape production is concentrated in the South, Southeast, and Northeast regions, where viticulture has socioeconomic importance. The states of Rio Grande do Sul and Santa Catarina (both parts of South Brazil) account for more than 90% of the national production of wines and juices. In Rio Grande do Sul state, the Serra Gaúcha region is a reference in viticulture, in which an expressive portion of the economic activity comes from grape cultivation and processing (AGOSTINI, 2011).

The commercial vine cultivars belong to the species *V. vinifera* (fine grapes) and *V. labrusca* (common grapes) or are hybrids of them (American grapes). The cultivars that are classified as common or rustic are used as feedstock for the production of table wines and juices, accounting for 80-90% of all grapes industrialized in Brazil (IBGE, 2020). Among these varieties, the 'Isabel' and 'Niagara' cultivars (both the white and





rose ones) highlight themselves. They are common table grapes, rustic, need less cultural practices, tolerant to fungal diseases, and adapt easily to wet climates (DETONI *et al.*, 2005).

The 'Isabel' variety is considered a hybrid cultivar, result of the crossing between *V. vinifera* and *V. labrusca* (*V. vinifera x V. labrusca*). Introduced in Rio Grande do Sul state between 1839 and 1842, this cultivar is considered the basis of Brazilian viticulture. Due to its rusticity, is capable of quickly adapt to the many climates of Brazil while presenting high productivity, with abundant harvests (CAMARGO et al., 2015). This grape variety currently represents about 40% of all grape produced in Rio Grande do Sul state (MELLO and MACHADO, 2020). Its main use is a feedstock in common red wines, grape juice, jellies, vinegar, and also being marketed *in natura*. Relative to Rio Grande do Sul state, the 'Isabel' cultivar accounted for 26.09% (10,000 ha) of the total vineyard area in 2015 (MELLO et al., 2017). The factors that favored the expansion of this cultivar throughout the region were the easy adaption to adverse climatic conditions and the high yield (MELLO et al., 2017).

According to Mello and Machado (2020), the 'Rose Niagara' variety arose as a result of a genetic mutation of the 'Niagara' grape in 1933; this cultivar is quite resistant to diseases, such as sour rot. The 'Niagara' is the result of the crossing of the 'Concord' grape, pollinated with the 'Cassady' variety. Therefore, the 'Niagara' grape is 75% *V. labrusca* and 25% *V. vinifera*, being a hybrid variety. This is one of the most consumed table grapes in Brazil, with a great expansion of the planted area in the last years due to the low production cost and high acceptance by the customers (DETONI *et al.*, 2005).

The production of wine and grape juice ends up generating large amounts of byproducts and wastes, in which the bagasse is the main residue. This bagasse is composed of seeds, peel, and the stalk. The grape seeds have oil, which can be extracted by pressing, solvent extraction, or supercritical extraction (GOWMAN et al., 2018; RAN et al., 2019). The waste from grape seed oil extraction is generally used as a component of animal food; however, due to the high fiber content, it is not possible to use it in large amounts. It is not recommended to dispose of/apply this waste in the soil because the biodegradability of the seeds is slow, and not all waste is converted to organic matter. The presence of residual oil in the waste also may have an impermeabilizing effect on soil, hindering water absorption, and movement through soil structure (FREITAS, 2007).

According to Menezes et al. (2015), the production of grapeseed oil from the wastes of wine and juice production may be an alternative to reduce the overall volume of byproducts, adding value to the process and the obtained materials, and generating new products with higher quality and price.

The quantity of seed in the grape berry varies; the seeds account for 2 to 5 wt.% of the total berry weight and have an edible oil content ranging from 10 to 20 wt.% (FREITAS, 2007). The grape seeds correspond to 14 to 17 wt.% of the weight of the bagasse; it has from 14 to 17 wt.% of oil, which varies according to the grape cultivar from which it is produced (OLIVEIRA, 2010).

One of the main motives for the commercial interest in the grapeseed oil is the high content of unsaturated fatty acids and linoleic acid (an []-6 polyunsaturated fatty acid), whose content in grape seed oil is approximately 70 wt.% higher than any other oil (ROCKENBACH *et al.*, 2010). According to Aresta *et al.* (2020), both the grapeseed oil and other byproducts, such as its flour and the grapeseed skin, have a high nutritional value, bright color, and a pleasant taste, however, these characteristics may change due to the grape cultivar used to obtain the oil.

Grapeseed oil is generally obtained by pressing or solvent extraction (solid-liquid extraction) or by seed pressing; however, other extraction techniques, such as supercritical extraction and ultrasound-assisted solvent extraction are also reported in the literature (ARESTA *et al.*, 2020; GOWMAN *et al.*, 2018; RAN *et al.*, 2019). The oil is a mixture of non-volatile lipidic substances (free or combined fatty acids), obtained after seed pressing or after solvent/supercritical extraction and subsequent solvent removal, when applicable (Li *et al.*, 2020).

Grapes are considered one of the best sources of phenolic compounds when compared to other fruits and vegetables. These compounds have antioxidant activity, which neutralizes free radicals. Some phenolic compounds, such as anthocyanins, contribute to the overall color, taste, aroma, and oxidative stability of the grapeseed oil and seed extracts. The acknowledgment of the antioxidant properties of the grapeseed oil, being it the result of the presence of fatty acid or phenolic compounds, has rendered a new overview of the possible health benefits of the consumption of this oil as a food component, or in the form of dietary or cosmetic products (CALDERÓN-OLIVER and LÓPEZ-HERNÁNDEZ, 2020; PEIXOTO et al., 2018).

According to Peixoto et al. (2018), phenolic compounds and fatty acids are mostly found in the internal layers of the seed; the content varies with the cultivar, being also influenced by environmental factors, harvest

conditions, storage, stage of maturation, among others. The extraction process (pressing, solvent extraction) also influences the extraction of these compounds from the seed.

The unsaturated fatty acids and phenolic compounds have, among other properties, the capacity to neutralize free radicals, presenting an antioxidant effect, such as resveratrol, which has an acknowledged antitumoral and cardioprotective effects due to the prominent antioxidant activity (BANEZ *et al.*, 2020). This property is inherent to several substances present in the grape, which confer to it and its products (wines, juices, seed/bagasse flour, and the seed oil) better quality and enhanced nutraceutical properties (OKINO-DELGA-DO *et al.*, 2018; ROCKENBACH *et al.*, 2010).

The antioxidant activity of fatty acids is believed to rely on the presence of unsaturations in the molecule. Since double bonds are less stable energetically compared to single bonds, unsaturated fatty acids tend to react with free radicals at the double bonds, breaking them and neutralizing the radical. Other possible mechanisms may involve reactions with metals and even the breaking of the carbon chain, but to a much smaller degree (BERBER et *al.*, 2014; CHOE and MIN, 2009).

Thus, the objective of the present work was to evaluate the seed oil yield from the 'Isabel' and 'Rose Niagara' grapes obtained by extraction with hexane, also evaluating the lipidic composition of the oils and their antioxidant activity.

### **Material and Methods**

The seed samples studied in this work were from the 'Isabel' (Vitis sp.) and 'Rose Niagara' cultivars (V. *labrusca x V. vinifera*), supplied by company Hugo Pietro (Caxias do Sul, Brazil), from the harvest 2018/2019. They were cleaned by sifting to remove bagasse and washed with tap water to remove impurities. Posteriorly, the material was dried at room temperature away from sunlight, packed in plastic bags, and kept refrigerated in a cold chamber  $(0\pm 2 \,^{\circ}C)$  until the preparation of the samples for analyses. The seeds were milled using a knife mill; the pulverized material was sifted using a mesh 9 sieve (mesh opening of 2.0 mm); the material that passed the sieve (i.e., smaller than 2.0 mm) was used in the extraction.

The seed oil was extracted by solid-liquid extraction, using hexane P.A. (99.9% purity, Dinâmica, Brazil) as the solvent and a glass Soxhlet apparatus with a chamber extraction volume of 200 mL; the hexane was used without further purification. Fifty grams (50 g) of seed powder were extracted with 500 mL hexane at  $65\pm3$ °C for 6 h. The condenser temperature was kept at  $10\pm2$  °C. Hexane was removed from the oil by rotary evaporation, using a Fisatom 802 rotary evaporator (Brazil), with a system pressure of 21 kPa and a condenser temperature of  $10\pm2$  °C. The rotary evaporation was kept for 1 h. The obtained oil samples were stored in amber glass flasks and kept refrigerated ( $4\pm2$  °C) until analysis.

The oil obtained after the extraction process and rotary evaporation was weighted to determine the essential oil yield, according to equation (1), proposed by Thiex *et al.* (2003) in the AOAC standard 2003.06:

$$Y = 100x(M_{0}/M_{s})(1)$$

In which 'Y' is the oil yield (wt.%); ' $M_s$ ' is the mass of seed (g) used in the extraction, and, ' $M_o$ ' is the mass of oil (g) collected after the removal of hexane.

Both qualitative and quantitative analyses were carried out following the procedures described by Agostini (2011). Qualitative analysis was carried out using a HP 6890 gas chromatograph equipped with HP-Chemstation software coupled to a HP MSD5973 mass spectrometer equipped with Wiley 275 spectra library. It was used a HP-Innowax (polyethylene glycol) capillary column (30 m x 250  $\mu$ m i.d.), with 0.25  $\mu$ m film thickness (HP, USA), with the following temperature program: 80 °C for 5 min, up to 230 °C at 3 °C·min<sup>-1</sup>, keeping at 230 °C for 30 min. Injector temperature was 230 °C, interface temperature of 310 °C, split ratio 1:25, helium as carrier gas at 40.0 cm·s<sup>-1</sup>, mass acquisition range of 45-550 m/z. It was injected 1  $\mu$ L of the sample, diluted in hexane in a 1:20 proportion.

Quantitative analysis was carried out using a HP 6890 gas chromatograph equipped with HP-Chemstation software and a flame ionization detector (FID). It was used a HP-FFAP capillary column (30 m x 250  $\mu$ m i.d.), with 0.25  $\mu$ m film thickness (HP, USA). The following temperature program was used: 100 °C for 5 min, up to 200 °C at 5 °C·min<sup>-1</sup>, then up to 230 °C at 3 °C·min<sup>-1</sup>, keeping at 230 °C for 30 min. Injector temperature was



230 °C, split ratio 1:30, detector temperature of 230 °C, hydrogen as carrier gas at 59.3 cm·s<sup>-1</sup>. It was injected I  $\mu$ L of the sample, diluted in hexane in a 1:20 proportion. For the quantification of the fatty acids present in the oil samples, heptadecanoic acid (C17) was used as an internal standard (1 g·L<sup>-1</sup>), which was added to the oil sample diluted with hexane (AGOSTINI, 2011).

The capacity of the oil samples to reduce the ABTS<sup>++</sup> radical was evaluated according to the procedures proposed by Rufino *et al.* (2007). The ABTS<sup>++</sup> radical was generated by reacting an aqueous solution of ABTS<sup>+</sup> (7 mmol·L<sup>-1</sup>) with an aqueous solution of potassium persulfate (140 mmol·L<sup>-1</sup>). This solution was kept in dark at room temperature for 12-16 h before use. Posteriorly, the ABTS<sup>++</sup> solution was diluted with ethanol 99% v/v, presenting an absorbance of 0.700±0.02 at 734 nm. 30.0  $\mu$ L of oil sample were added to 3.0 mL of the diluted ABTS<sup>++</sup> solution; the absorbance was measured after exactly 6 min after mixing. It was used a Micronal B-542 UV/Vis spectrophotometer, with a resolution of 0.001 abs and measurement range of 0.000-3.000 abs. The results were expressed as a percentage of scavenging of ABTS<sup>++</sup> radical and as milliequivalents of Trolox antioxidant activity.

The treatments were the grape varieties ('Isabel' and 'Rose Niagara'), with five replicates for each treatment. The yield, lipid composition, and antioxidant activity data underwent analysis of variance (ANOVA) and the means were compared by Tukey's multiple range test at 5% probability ( $\alpha = 0.05$ ). The data was analyzed using AgroEstat<sup>®</sup> software.

## **Results and Discussion**

## Seed oil yield

According to Table 1, there was a statistical difference between the two studied grape cultivars regarding the seed oil yield. The 'Isabel' grape seed has had a higher yield than the range reported by Agostini (2011). Relative to 'Rose Niagara' seeds, the observed yield was 23.15 wt.%, quite superior to the range proposed by the same author.

| Table I – Seed oil yield of the 'Rose Niagara' and 'Isabel' grapes, obtained by Soxhlet extraction with hexane for 6 h. |                       |  |
|---|-----------------------|--|
| Cultivar  | Seed oil yield (wt.%) |  |
| 'Rose Niagara'  | 23.15 a               |  |
| 'Isabel'  | 19.12 ь               |  |
| Coefficient of variation (%)  | 2.05                  |  |

Means followed by the same letter do not present statistical difference by Tukey's multiple range test at 5% probability ( $\alpha = 0.05$ ). Source: authors (2020).

According to Agostini (2011), the seed oil content may range from 13.0 and 18.4 wt.% among the many American and hybrid grape varieties. The white grapes present a seed oil content that ranges between 13.5 and 16.5 wt.%; the seed oil content in red grapes is generally in the range of 13.0 and 18.4 wt.%. Oliveira (2010) cites that grape seed may contain between 14.0 and 17.0 wt.% of oil, depending on the variety.

According to Martin *et al.* (2020), the overall grape seed oil yield is highly dependent on the grape cultivar; its range lies within 6.0 and 23.0 wt.%. The 'Isabel' cultivar generally has an oil content of 11.4-13.2 wt.%, considering Soxhlet extraction using hexane (AGOSTINI, 2011). Freitas (2007) reported a seed oil yield of 7.4 wt.% for 'Isabel' grapes. Santos *et al.* (2011) reported a seed oil yield of 10.84 and 11.53 wt.% for 'Isabel' and 'Rose Niagara' grapes, using a methanol/chloroform mixture as the extracting solvent. Aver *et al.* (2019), studying the effect of granulometry and extraction time on the obtainment of seed oil from 'Isabel' grapes, reported a yield of 19.02 wt.% for an extraction time of 6 h and a particle size of 0.25 mm (mesh 60), these conditions maximized the oil yield. Berradre *et al.* (2016) reported an oil yield of 8.60±0.34 wt.% for 'Malvasía' grapes seeds extracted with hexane for 6 h. Wada *et al.* (2018) reported an oil yield of 11.1±0.9 wt.% and 13.9±0.5 wt.% for the seeds of 'Noble' and 'Carlos' muscadine grapes, extracted using hexane.

Considering Soxhlet extraction, it can be seen that the 'Rose Niagara' variety presented a higher yield than the 'Isabel' grape and also above the overall mean of the yields reported by the literature. The Brazilian viticulture uses mainly the hybrid grapes (such as the 'Isabel', among others) as feedstock to obtain seed oil.

However, only the varieties from *V. vinifera* are currently used in the obtainment of grape seed oil (SHINAGA-WA et al., 2015).

According to Agostini (2011) and Martin *et al.* (2020), yield differences between the cultivars may arise due to the physiological maturation of the grape, edaphoclimatic factors, and also due to seasonality. This may explain the observed differences, especially regarding the 'Rose Niagara' grape.

## Seed oil chemical composition

According to the GC analyses, there were differences in the lipidic composition of the seed oil of the studied cultivars. Table 2 compiles the chemical composition of both oils.

| able 2 – Chemical composition (wt.%) and main characteristics of the fatty acids that composed the seed oil of the 'Isabel' an<br>'Rose Niagara' grapes, obtained by Soxhlet extraction with hexane. |              |                             |                |                |  |
|--|--------------|-----------------------------|----------------|----------------|--|
| Commonweak   | Codification | Classification —            | Content (wt.%) |                |  |
| Compound   | Codification |                             | 'Isabel'       | 'Rose Niagara' |  |
| Palmitic acid  | C16:0        | saturated                   | 15.47 a        | 5.80 b         |  |
| Stearic acid   | C18:0        | saturated                   | 42.51 a        | 10.97 Ь        |  |
| Oleic acid   | C18:1        | $\omega$ -9 monounsaturated | 22.07 Ь        | 72.08 a        |  |
| Linoleic acid  | C18:2        | $\omega$ -6 polyunsaturated | 19.96 a        | 11.15 b        |  |

Means in row followed by the same letter do not present statistical difference by Tukey's multiple range test at 5% probability ( $\alpha = 0.05$ ). Source: authors (2020).

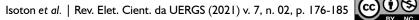
By verifying Table 2, it can be seen that there was a difference in the composition of the two extracted seed oils. The main interest in grape seed oil is due to its high content of unsaturated fatty acids. One of the most important is the linoleic acid (C18:2), which compose roughly 60-75 wt.% of the seed oil, however, the exact content depends on several factors and also on the cultivar used in the obtainment. Linoleic acid is absent in most oil, such as soybean, cotton, and corn oils (OLIVEIRA, 2010).

Significant differences were observed between the cultivars in the present work, in both yield and chemical composition. According to Martin et al. (2020), there is high variability between grape cultivars relative to both seed oil content and composition. Regarding oil composition, is noteworthy the high content of oleic acid in the 'Rose Niagara' seed oil (72.08 wt.%), compared to the 'Isabel' grape oil (22.07 wt.%). The small amounts of linoleic acid (19.96 and 11.15 wt.% in 'Isabel' and 'Rose Niagara' grapes, respectively), quite smaller than the literature range, also deserve highlight.

Rockenbach *et al.* (2010) cited that oleic acid, whose content in the 'Isabel' grape seed oil was 13.07 wt.%, provides oxidative stability to the oil. The same authors reported the following composition range of grapeseed oil from both *V. vinifera* and *V. labrusca*: 2.89-4.08 wt.% stearic acid, 6.17-8.46 wt.% palmitic acid, 9.48-16.81 wt.% oleic acid, and 47.63-60.02 wt.% linoleic acid. Aver *et al.* (2019) reported the following composition for 'Isabel' seed grape oil, obtained by Soxhlet extraction with hexane: 87.91 wt.% linoleic acid, 7.46 wt.% oleic acid, and 4.63 wt.% palmitic acids. Dedebas *et al.* (2020) reported the following composition for cold-pressed grape seed oil: palmitic, stearic, oleic, linoleic, and linolenic acid; linoleic acid was the main component of the seed oil (63.85 wt.%). Freitas (2007) reported a palmitic acid content of 9.43 wt.%, 22.8 wt.% of oleic acid, 4.82 wt.% of stearic acid, and 62.2 wt.% of linoleic acid in the seed oil from 'Isabel' grapes. The same author also cited that oleic acid content was higher in the 'Isabel' seed oil obtained by Soxhlet extraction.

Relative to the observed results, linoleic acid, which was mostly found in the literature, is a minor compound in the obtained oil from 'Isabel' grapes (19.96 wt.% in the present work against <40.00 wt.% in other works). On the other hand, oleic acid composed most of the seed oil of 'Rose Niagara' grapes (72.08 wt.%); this compound was present in amounts smaller than 20 wt.% in other studies. These remarkable differences in the oil compositions may be a result of differences between the cultivars (variability), cultivation management, soil type, and the edaphoclimatic conditions, among other factors (SHINAGAWA *et al.*, 2015; PEIXO-TO *et al.*, 2018).

Polyunsaturated fatty acids are essential to the human body because they cannot be synthesized by the organism. Thus, grapeseed oil is a valuable source of these compounds. Studies showed that grape seed oil



has pharmacological properties that benefit the health, such as the protective and antioxidant effect on LDL proteins (ROCKENBACH et al., 2010).

Linoleic acid, considered one of the major fatty acids that compose grapeseed oil, was present in smaller amounts in the oils obtained in the present work than the ranges cited by Rockenbach *et al.* (2010) and Shinagawa (2015); nevertheless, the oil from the 'Isabel' grapes has presented a higher amount of linoleic acid (19.6 wt.%) than the one from the 'Rose Niagara' grapes (11.15 wt.%).

Comparing the literature data with the ranges reported by FAO (2019), it can be seen that there is a very high variation degree between the contents (5.5-11.0 wt.% for palmitic acid, 3.0-6.5 wt.% for stearic acid, 12.0-28.0 wt.% for oleic acid, and 58.0-78.0 wt.% for linoleic acid). This may be attributed to environmental factors, cultivar, harvest, and other factors that may interfere in the fatty acids production and accumulation in the grape seed. Another factor that has importance is the extraction kind and its parameters, such as the solvent used, feedstock particle size, and also the time of the extraction process (AVER *et al.*, 2019; FREITAS, 2007).

# Seed oil antioxidant activity

By analyzing Table 3 it is possible to verify that the difference between the antioxidant activity of the oils was significant. The results of the tests of antioxidant activity of both oils are presented in Table 3.

| Cultiver                     | Antioxidant activity               |                          |  |  |
|------------------------------|------------------------------------|--------------------------|--|--|
| Cultivar                     | % of ABTS <sup>++</sup> scavenging | µM equivalent of Trolox® |  |  |
| 'Isabel'                     | 22.11 a                            | 26.8 a                   |  |  |
| 'Rose Niagara'               | 20.85 ь                            | 26.2 b                   |  |  |
| Coefficient of variation (%) | 2.03                               | 1.18                     |  |  |

Means followed by the same letter do not present statistical difference by Tukey's multiple range test at 5% probability ( $\alpha = 0.05$ ). Source: authors (2020).

This activity, by the chemical composition, may not be associated solely with oleic acid (monounsaturated fatty acid), which composed approximately 72 wt.% of the 'Rose Niagara' seed oil. In this sense, the antioxidant may be associated with the presence of linoleic acid (Ali *et al.*, 2012; Elagbar *et al.*, 2016), which is a polyunsaturated fatty acid (roughly 20 wt.% in the 'Isabel' seed oil and roughly 11 wt.% in the 'Rose Niagara oil), once no phenolic compounds were detected in the samples analyzed by GC. However, Chen *et al.* (1997) have cast doubt on the antioxidant activity of linoleic acid; in this sense, a synergistic effect may also play a role in the overall antioxidant activity of the oil.

It can be seen that these values are considered below most values reported by other studies. Dedebas et al. (2020) reported antioxidant activity of 4.89 mM equivalent of Trolox (1.292  $\mu$ g·mL<sup>-1</sup>) for grapeseed oil obtained by cold pressing and stored at 20 °C. Ghafoor et al. (2020) reported antioxidant activities in the range of 78-92% of ABTS<sup>+</sup> scavenging for several grape seed oils from Turkey. On the other hand, Li et al. (2020) reported an antioxidant activity of 13.0  $\mu$ M equivalent of Trolox for grape seed oil obtained by Soxhlet extraction with hexane. This may be likely due to differences in the chemical composition, the extraction process, or the lack of detectable phenolic compounds.

However, it is also important to highlight that phenolic compounds are generally extracted using a mixture of polar solvents (hydroalcoholic solutions in the range of 50-70% v/v ethanol or methanol) (ANATASOV et al., 2019; PEZZINI et al., 2019). These compounds, due to the low volatility, are generally analyzed by HPLC, although analysis by GC is possible after proper sample preparation, such as analyte derivatization (PEREDO et al., 2021; TAO et al., 2014).

The literature cites the presence of E vitamin (tocopherols) as one of the substances with the greatest contribution to the antioxidant activity of grape seed oil. However, E vitamin is prone to decomposition, which ends up reducing the overall antioxidant activity of the oil. The early stages of winemaking may also play an important role in the degradation of the antioxidant compounds in the grape seed and pomace (BANEZ et al., 2020; OKINO-DELGADO et al., 2018).

# Conclusions

There were differences in the oil yield between the cultivars, in which the 'Rose Niagara' has presented a yield of 23.15 wt.%, whereas the 'Isabel' grape has had a yield of 19.12 wt.%. The chemical composition of the obtained oils also was significantly different; it was observed a high oleic acid content in the 'Rose Niagara' seed oil (72.08 wt.%); the main compound of the 'Isabel' seed oil was stearic acid (42.51 wt.%). Both oils presented a low antioxidant activity; however, there was a statistical difference between the varieties, in which the 'Isabel' seed oil has had higher antioxidant activity than the 'Rose Niagara' seed oil. Considering the small difference in the antioxidant activity of the two seed oils and the higher oil yield, seeds from the 'Rose Niagara' cultivar may also be considered as a possible source of oil for use in food, cosmetics, and pharmaceutical industries.

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