REVISTA DELOS DESARROLLO LOCAL SOSTENIBLE

Characterization of green mandarin peel essential oil extracted by laboratory and industrial methods

Caracterização do óleo essencial de casca de tangerina verde extraído por métodos laboratoriais e industriais

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ABSTRACT
This study aimed to evaluate the yield and chemical composition of the essential oil of immature fruits of C. deliciosa varieties cultivated in Rio Grande do Sul using laboratory (hydrodistillation) and industrial (scarification) methods. During the period of industrial processing (scarification), fruits from the same batches were sampled for laboratory hydrodistillation. Essential oil yield and chemical composition were evaluated by GC/MS and GC-FID The average yield obtained was 0.07 wt.% (hydrodistillation) and 0.53 wt.% (scarification). EO yield followed a quadratic model regarding sample collection time in both methods, indicating an optimum time for fruit collection regarding EO yields. According to EO characterization, 24 different compounds were identified in hydrodistillation and 19 in scarification. The major compounds detected were limonene (66.5 – 71.3 wt.%) and γ-terpinene (12.1 – 18.4 wt.%), regardless of the extraction method. A greater number of compounds with content above 1.0 wt.% was found in the oil obtained by hydrodistillation. The scarification method provided greater extraction yield and a smaller number of compounds relative to the essential oil of mandarins extracted by hydrodistillation.

Keywords: citrus deliciosa, chemical composition, yield, scarification, hydrodistillation.

RESUMO
Este trabalho teve como objetivo avaliar o rendimento e a composição química do óleo essencial de frutos imaturos de variedades de C. deliciosa cultivadas no Rio Grande do Sul, utilizando os métodos laboratorial (hidrodestilação) e industrial (escarificação). Durante o período de processamento industrial (escarificação), frutos dos mesmos lotes foram amostrados para hidrodestilação em laboratório. O rendimento em óleo essencial e a composição química foram avaliados por GC/MS e GC-FID. O rendimento médio obtido foi de 0,07 wt.% (hidrodestilação) e 0,53 wt.% (escarificação). O rendimento dos OEs seguiu um modelo quadrático em relação ao

tempo de recolha das amostras em ambos os métodos, indicando um momento ótimo para a recolha dos frutos em relação ao rendimento dos OEs. De acordo com a caraterização dos OEs, foram identificados 24 compostos diferentes na hidrodestilação e 19 na escarificação. Os principais compostos detectados foram o limoneno (66,5 - 71,3 wt.%) e o γ-terpineno (12,1 - 18,4 wt.%), independentemente do método de extração. No óleo obtido por hidrodestilação foi encontrado um maior número de compostos com teor superior a 1,0 wt.%. O método de escarificação permitiu um maior rendimento de extração e um menor número de compostos em relação ao óleo essencial de tangerina extraído por hidrodestilação.

Palavras-chave: citrus deliciosa, composição química, rendimento, escarificação, hidrodestilação.

1 INTRODUCTION

Citriculture is one of the most important agricultural production chains in Brazil, which according to Neves and Trombini (2017) generates an income of US$ 6.5 billion per year in all links of its chain, providing more than 200,000 jobs directly and indirectly. The country is responsible for more than half of the worldwide orange juice production and for 76 % of the world trade of this commodity. In the Citrus processing industry, the production of essential oils has shown its importance, placing Brazil among the main suppliers of Citrus essential oil in the world market (Bizzo et al., 2009). In 2019, the country surpassed the mark of 56.000 t of essential oils from citrus plants exported, generating an income of around US$ 301 million (FAO, 2018).

Citrus essential oils are widely used in the food, pharmaceutical, and cosmetic industries, as natural flavoring substances that enhance organoleptic sensations (taste and aroma) of several products (Cornélio et al., 2004). In the food industry alone, Citrus essential oils represent 40 % of the total essential oils employed (Ferrua et al., 2001). Among the compositions (blends), the oils of bergamot, lemon, mandarin, and orange are the most commercialized worldwide for perfumery (Bizzo et al., 2009).

Different methods can be used for the extraction of essential oils. However, depending on the method used, the composition of the oils can vary considerably (Cassel et al., 2009). Among the extraction methods used to obtain essential oils from Citrus fruits on an industrial scale, cold pressing and scarification are the most used. These techniques cover a widely used mechanical extraction method in the juice industry, through which the ripe fruits are pressed, and both juice and essential oil are extracted and separated by centrifugation (Oliveira and José, 2009).

In Rio Grande do Sul state, the technique commonly used for the extraction of essential oils from Citrus fruits differs from the one used in Southeast Brazil because immature (unripe) mandarin fruits collected during thinning stage undergo a process of scarification of the epicarp. The oil obtained in this process is decanted and centrifuged, thus giving rise to the so-called "green mandarin oil", which is highly valued in the international market for uses in perfumery and cosmetics (Ecocitrus, 2015).

The extraction of the green mandarin essential oil is made from fruits removed by means of a management practice usually applied in mandarin trees in the region, which is the manual thinning of fruits. This technique aims to reduce alternate bearing in mandarin trees, as well as to improve the quality of the fruits through an increase in the size and enhancement of the organoleptic characteristics (Köller, 2009; Rodrigues et al., 1998). Considering that Citrus production in Rio Grande do Sul is mainly intended for fresh consumption, this practice is very important in the management of Citrus orchards (João and Conte, 2018). Thus, the commercialization of fruits for the extraction of essential oils allows for an economic return of part of the expenses that citrus growers have with labor to carrying out the thinning (Schwarz and Köller, 1991; Oliveira et al., 2009).

Hydrodistillation is among the oldest the essential oil extraction methods, considered a craft method, nevertheless, widely used on a laboratory scale (Silveira et al., 2012). In this technique, the raw material remains immersed in boiling water and the volatile compounds are distilled, using a Clevenger-type apparatus as the condenser and separator. This method proved to be extremely versatile and can be used to extract small amounts of essential oils from different types of plant structures: flowers, fruits, leaves, rhizomes, roots, seeds, barks, chestnuts, and branches (Silveira et al., 2012). However, hydrodistillation has limitations due to losses by hydrolysis and solubilization of substances, evaporation of volatile compounds and trapping of aromatic molecules in the sample plant material and the cooking water (Darjazi, 2015; Waheed et al., 2020). According to Waheed et al. (2020), the efficiency of the hydrodistillation is quite variable, depending on several factors that range from the moisture content of the plant material to the power of the heat source.

The 'Montenegrina' mandarin tree is a *Citrus deliciosa* Tenore cultivar with the largest acreage in the State of Rio Grande do Sul, although there are significant areas occupied by other cultivars of this species, as for example the 'Caí', 'Pareci', and 'Rainha cultivars (Oliveira et al.,

2018). According to Frizzo et al. (2004), the composition of the essential oil of the 'Cai' and 'Montenegrina' mandarins are chemically similar to those of the Italian mandarin essential oil, an oil of greater value and commercial interest. Therefore, Rio Grande do Sul state has a great potential for the production of essential oil with high quality and added value, in view of the predominance of the cultivation of mandarin trees of the species *C. deliciosa* in the region, as well as the presence of companies that work with juice and essential oil extraction.

Due to the widespread use of laboratory and industrial extraction methods and the predominance of the production of *C. deliciosa* mandarin trees, this study aimed to compare the extraction yield and composition of essential oils extracted from *Citrus deliciosa* Tenore fruits from the same batches. The methods of hydrodistillation, representing a laboratory scale, and extraction by scarification, to represent an industrial scale, were carried out using whole *C. deliciosa* fruits, aiming to verify differences in the essential oils obtained by both methods.

2 MATERIAL AND METHODS

2.1 FUIT SAMPLING

Samples of immature *C. deliciosa* fruits were collected in the Agroindustry of Juices and Essential Oils located in Montenegro, Rio Grande do Sul state, on 2017-03-14, 2017-03-21, 2017-03-28, and 2017-04-04, with three samples weighing approximately one kilogram (1.0 kg) of fruits from the same batch being collected on each date. Three samples of the essential oil obtained in the Agroindustry were also collected through the scarification of the fruit peel, decantation, and centrifugation, from the same batches from which the fruit samples were collected. The sampling period corresponded to the moment when producers obtain the highest return by the industry, as well as the time closest to that recommended for the thinning of mandarin trees. The batches of fruits from the Agroindustry corresponded to mixtures of *Citrus deliciosa* cultivars grown in Vale do Caí, Rio Grande do Sul state, which are the 'Montenegrina', 'Caí', 'Pareci' and 'Rainha' ones.

2.2 HYDRODISTILLATION PROCEDURE

The fruit samples collected in the agroindustry were taken to the laboratory, where they were submitted to hydrodistillation using a Clevenger-type apparatus. The fruits were cut into four parts, put into round-bottom distillation flasks with a capacity of 6 L and filled with 2 L of

distilled water. The extraction procedure lasted for 4 h. The essential oil extracted was measured in the graduated column of the apparatus, weighed using an analytical balance, and then transferred to amber bottles with a capacity of 10 mL with the aid of a precision pipette for storage until the moment of analysis.

2.3 CHROMATOGRAPHIC ANALYSIS

GC/MS analysis was performed on a HP 6890 gas chromatograph coupled to a HP MSD5973 mass spectrometer equipped with the HP-Chemstation software and the Wiley 275 spectra library (Hoboken, NJ, USA). An HP-5 fused-silica capillary column (30 m x 250 µm) with 0.50 µm film thickness (Hewlett Packard) was used. The temperature programming used was from 60 °C to 246 °C at 3 °C·min^{-1}, injector temperature of 250 °C, interface temperature of 280 °C; split ratio 1:100; helium as carrier gas (56 kPa); flow rate of 1.0 mL·min^{-1}; ionization energy of 70 eV; injected sample volume of 1 µL, diluted in hexane (1:10).

The components were identified by comparing their respective mass spectra with those of the Wiley spectra library, selected by the system software by similarity percentage and by comparing their linear retention indices (LRI) with those reported by Adams (2017). The LRI of the components was calculated using the Van den Dool and Kratz equation, using a standard solution of alkanes ranging from C7 to C30.

GC/FID analysis was performed using a Hewlett Packard 6890 Series gas chromatograph equipped with an HP-Chemstation data processor, using an HP-5 column (30 m × 320 µm i.d.) with 0.50 µm film thickness (Hewlett Packard, Palo Alto, CA, USA). Temperature programming was the same as for GC-MS; injector temperature of 250 °C; 1:50 split ratio; detector temperature of 250 °C; hydrogen as carrier gas (34 kPa); injected sample volume of 1 µL, diluted in hexane (1:10). 1-octanol was used as an internal standard, at a concentration of 30.22 g·L^{-1}, being injected 0.1 µL with the EO samples.

2.4 DATA ANALYSIS

The frequency of the identified components, extracted by different methods on different dates, was subjected to factorial variance analysis (two extraction methods × four sampling dates). Pearson's linear correlation analysis (r) was also performed for the contents of essential oils and their different compounds, using the SAS 9.4® software. Additionally, a regression

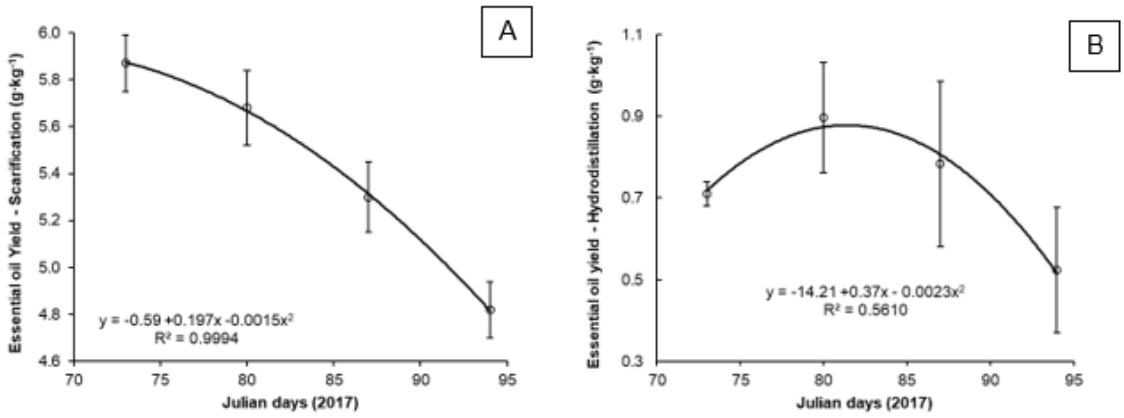
analysis of the contents of the components in the essential oils extracted by hydrodistillation and scarification was carried out, using the Sigmaplot® 14.0 software.

3 RESULTS AND DISCUSSION

3.1 EXTRACTION YIELD OF THE ESSENTIAL OILS

Regarding the essential oil yield, a quadratic behavior relative to time was observed for both evaluated methods (Figures 1A and 1B). In the scarification method, the EO yield decreased over the period evaluated, with the highest values obtained being 0.59 wt.% in the first evaluation at 73 Julian days (March 14) (Figure 1A). The yield of oil extracted by hydrodistillation reached a maximum value of 0.09 wt.% at 80 Julian days (March 21), with a decreasing behavior from this point on (Figure 1B).

Figure 1. Regression analysis of essential oil yield obtained by scarification (A) and hydrodistillation (B) according to the sampling date (Julian days). Montenegro, RS, April 2017.



The Pearson's linear correlation coefficient calculated between the two extraction methods was r = 0.70, however there was no statistical significance (p = 0.30), demonstrating that there was no correlation of the levels extracted between the two methods. The extraction yields varied in the evaluated period on average between 4.82 g·kg^{-1} and 5.87 g·kg^{-1} of citrus fruits for the industrial method of scarification, and range 0.52 g·kg^{-1} and 0.90 g·kg^{-1} for hydrodistillation.

According to Pauletti and Silvestre (2018), industrial extraction yields are variable, and for green mandarin essential oil (*C. deliciosa*), they vary from 4.0 g·kg^{-1} to 5.0 g·kg^{-1} of fruit processed. In this study, an average yield of 5.4 g·kg^{-1} was obtained in the industrial extraction.

Calculating the content of essential oil contained in the fruits, it varied from 0.48 wt.% to 0.58 wt.% by scarification, and from 0.04 wt.% to 0.10 wt.% by hydrodistillation. Frizzo et al. (2004), comparing steam distillation and scarification, reported yields of 0.45 wt.% and 0.60 wt.%, respectively, for all samples collected during one season. Thus, the yield obtained in the present study is very close to that previously verified in the southern region by these authors.

It is known that the efficiency of hydrodistillation can vary according to factors such as the type of plant material, particle size or porosity, nature of the bioactive compounds to be extracted, and the thermodynamic characteristics of the solvent used (usually water) (Waheed et al., 2020). According to Teixeira et al. (2014), the levels of essential oil in *C. deliciosa* peels vary from 0.25 % v/w to 1.29 % v/w when extracted by hydrodistillation in a Clevenger-type apparatus. However, the yield obtained in this study by the same method is lower than what was reported by these authors, being similar to the values reported by Simas et al. (2015) for 'Mexerica-do-Rio' (*C. deliciosa*), with an essential oil yield of 1.99 % v/w for hydrodistillation. However, these authors evaluated ripe fruits only, not analyzing the contents during development, such as immature fruits, as in the case of this study. In addition, the fruits evaluated in the work of Simas et al. (2015) were grown in another region of the country (Southeast Brazil). According to Guenther (1948), green fruits provide EO of higher quality in terms of aroma compared to the EO of ripe fruits, especially concerning cosmetics and perfumery applications.

3.2 CHEMICAL COMPOSITION OF THE ESSENTIAL OILS

Twenty-five different volatile compounds were identified in the essential oil analyzed in this experiment, with the oils extracted by hydrodistillation being those that presented the greatest number of substances (24), compared to scarification (19) (Table 1). The identified compounds corresponded to up to 99.97 % of the total composition of essential oil extracted by scarification, and up to 95.07 % of the total oils extracted by hydrodistillation.

The major compounds in the EOs obtained by scarification (S) and hydrodistillation (C) methods were the monoterpenes limonene 66.53 wt.% (S) - 71.28 wt.% (C); and γ-terpinene, 12.09 wt.% (S) - 18.42 wt.% (C) (Table 1). The other major compounds in scarification were: myrcene (1.75 wt.%), sabinene (1.67 wt.%), terpinolene (1.06 wt.%), and α-thujene (0.70 wt.%) - all monoterpene hydrocarbons. This chemical class was responsible for more than 98 % of the total composition of the essential oil extracted by this method on average (Table 2); whereas in

hydrodistillation, in addition to monoterpene hydrocarbons, chemical classes such as alcohols (linalool – 1.37 wt.%, α-terpineol – 5.06 wt.%, and terpinen-4-ol – 2.14 wt.%), amines, esters (methyl N-methylanthranilate – 2.51 wt.%), in addition to aldehydes, have had important contributions to the composition of the EO obtained (Table 1).

The results obtained in this work were similar to those reported by Frizzo et al. (2004) who studied the EO of *C. deliciosa* fruits grown in the same region and obtained by the same extraction methods, with limonene among the major compounds mentioned by these authors, with average contents of 73.36 wt.% (C) - 72.18 wt.% (S) and γ-terpinene, whose contents were 14.75 wt.% (C) - 17.94 wt.% (S). As in this study, Frizzo et al. (2004) obtained methyl N-methylanthranilate as one of the major compounds in hydrodistillation, and also myrcene, α-pinene, β-pinene, octanal, and terpinen-4-ol among the most abundant compounds.

Table 1. Chemical composition of the essential oils (wt.%) identified by sample date (Julian days) and extraction method, probabilities of significance of the analysis of variance (F test) for time (Pt), method (Pm), and for interaction (Pt*m), and Pearson´s correlation coefficients. Montenegro, RS, April 2017.

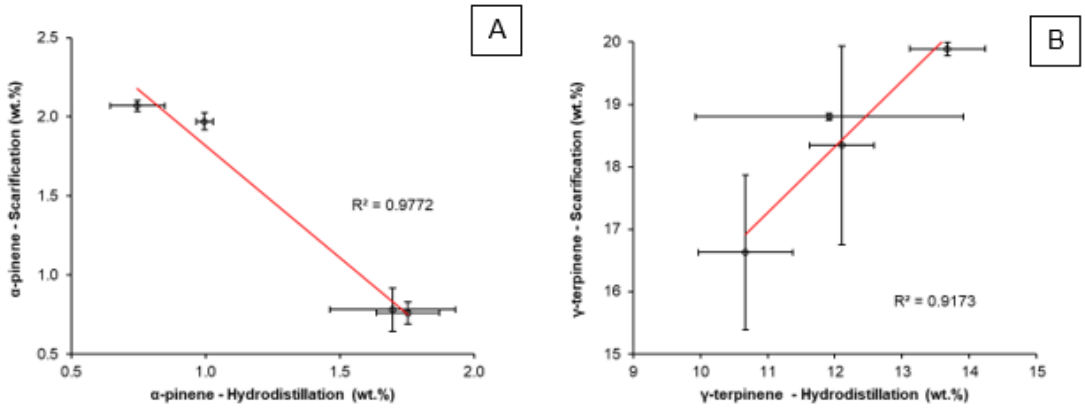
Component	Scarification										Hydrodistillation										P t (date)	P m (method)	P t*m (date*method)	Pearson´s Correlation		
	14-mar (73)		21-mar (80)		28-mar (87)		4-abr (94)		Mean		14-mar (73)		21-mar (80)		28-mar (87)		4-abr (94)		Mean					r	p	
limonene	71.14		70.15		71.63		72.20		71.28	A	67.06		66.69		66.21		66.16		66.53	B	0.95	0,00	0.80	-0.64	0.37	NS
γ-terpinene	18.80		19.89		18.34		16.63		18.42	A	11.92		13.68		12.10		10.67		12.09	B	0.01	<0.0001	0.89	**0.96**	**0.04**	*
myrcene	1.82	aA	1.77	aA	1.73	aA	1.68	aA	1.75		1.28	aB	1.37	aB	1.08	bB	1.16	bB	1.22		0.00	<0.0001	0.02	0.59	0.41	NS
sabinene	1.75		1.73		1.64		1.58		1.67	A	0,77		0.69		0.54		0.56		0.64	B	0.04	<0.0001	0.88	0.91	0.09	NS
α-pinene	2.07	aA	1.97	aA	0.78	bB	0.76	bB	1.40		0.75	bB	1.00	bB	1.70	aA	1.75	aA	1.30		0.01	0.06	<0.0001	**-0.99**	**0.01**	*
terpinolene	1.01	abB	1.07	abB	1.21	aA	0.95	bB	1.06		1.58	aA	1.37	abA	1.00	cA	1.20	bcA	1.29		0.00	<0.0001	<0.0001	-0.57	0.43	NS
α-thujene	0.76	aA	0.73	aA	0.66	aA	0.66	aA	0.70		0.09	bB	0.22	aB	0.19	aB	0.16	aB	0.17		0.11	<0.0001	0.01	-0.41	0.59	NS
cis-β-bergamotene	0.52		0.63		0.56		0.66		0.59		0.61		0.57		-		-		0.29		0.63	0.17	0.54	-0.31	0.68	NS
α-sinensal	0.42		0.44		0.42		0.51		0.45	A	0.08		0.06		0.12		0.06		0.08	B	0.81	<0.0001	0.46	-0.53	0.47	NS
α-terpinene	0.40		0.40		0.50		0.33		0.41	B	0.47		0.64		0.69		0.61		0.60	A	0.42	0,01	0.75	0.44	0.56	NS
δ-cadinene	0.29		0.31		0.32		0.35		0.32	A	-		0.06		-		-		0.02	B	0.44	<0.0001	0.32	-0.14	0.87	NS
linalool	0.20		0.32		0.27		0.35		0.29	B	1.41		1.17		1.37		1.53		1.37	A	0.41	<0.0001	0.43	0.03	0.97	NS
α-terpineol	0.28		0.30		0.24		0.33		0.29	B	4.95		4.54		4.70		6.07		5.06	A	0.34	<0.0001	0.41	0.69	0.31	NS
terpinen-4-ol acetate	0.09		0.09		0.10		0.13		0.10	B	1.39		1.09		0.93		1.32		1.18	A	0.24	<0.0001	0.27	0.23	0.77	NS
octyl acetate	0.08		0.13		0.11		0.00		0.08		0.16		0.19		0.05		0.16		0.14		0.61	0.21	0.46	0.19	0.81	NS
octanal	0.20	aB	-	aB	0.09	aB	0	aB	0.07		2.55	aA	1.21	cA	1.08	cA	1.47	bA	1.58		0.00	<0.0001	0.00	0.79	0.21	NS
β-caryophylene	0.05		0.04		0.10		0.07		0.07		-		-		-		-		-		-	-	-	-	-	-
limonene oxide	-	bA	-	bA	0.17	aA	-	bA	0.04		0.09	aA	0.04	aA	-	aB	0.07	aA	0.05		0.21	0.77	0.00	-0.82	0.19	NS
germacrene-D	-		-		0.03		0.05		0.02		-		0.08		-		-		0.02		0.72	1.00	0.30	-0.55	0.45	NS
methyl N-methylanthranilate	-		-		-		-		-		1.81		1.82		3.10		3.30		2.51		-	-	-	-	-	-

terpinen-4-ol	-	-	-	-	-	2.02	1.99	2.22	2.33	2.14	-	-	-	-	-	-
neryl formate	-	-	-	-	-	0.46	0.56	0.21	0.33	0.39	-	-	-	-	-	-
nerol	-	-	-	-	-	0.24	0.31	0.31	0.46	0.33	-	-	-	-	-	-
camphor	-	-	-	-	-	0.17	0.26	0.19	0.52	0.28	-	-	-	-	-	-
camphene	-	-	-	-	-	0.07	0.03	0.01	-	0.03	-	-	-	-	-	-
Total identified	99.88	99.97	98.70	97.20	98.94	95.07	94.54	91.76	92.89	93.57	-	-	-	-	-	-

*Capital letters compare the effect of the extraction method, either on the average of each compound or across samples; and lowercase letters express the effect of time, using the same method. NS – not significant at 5 % error probability. The chromatograms of the essential oils obtained by hydrodistillation and scarification with peak identification are available as supplementary material.

The contents of most compounds had no significant correlation with the extraction methods used, with exception of γ-terpinene and α-pinene, whose correlations were significant (Table 1). For γ-terpinene, a strong positive linear correlation was observed (r = 0.96), in both methods (Figure 2A); while for α-pinene the correlation was strongly negative (r = -0.98) (Figure 2B).

Figure 2. Correlation analysis between the contents of γ-terpinene (A) and α-pinene (B) according to the extraction methods used (scarification and hydrodistillation). Montenegro, RS, April 2017.



3.3 INFLUENCE OF THE EXTRACTION METHOD ON ESSENTIAL OIL YIELD AND COMPOSITION

The interaction between the identified components, extraction methods used and the harvest date, as well as the interactions between the methods (Table 1) were also evaluated. The interaction between the levels of γ-terpinene and the sampling time was significant, given that the contents of this compound increased. There was also a significant relationship between the levels of α-pinene and the variables time and method, with increasing levels of α-pinene being extracted via hydrodistillation and decreasing in scarification.

According to Pauletti and Silvestre (2018) and Dugo and Mondello (2011), mandarins have higher yield and variability in terms of essential oil composition compared to those from other Citrus fruits. In these fruits, aldehydes, alcohols, and ketones, commonly present as minor compounds or even as trace compounds, are very important in composing the aroma of the essential oil. Thus, these compounds have higher added value when compared to other terpenes that compose the essential oil (Pauletti and Silvestre, 2018). In the present study, the highest

levels of alcohols, amines, esters, and aldehydes were obtained by hydrodistillation (Table 2). This method also provided the greatest diversity of substances in the essential oil composition. According to Cassel et al. (2009), the extraction method used is decisive in the essential oil composition, impacting directing its quality.

Table 2. Average chemical composition (wt.%) of essential oils extracted by industrial (scarification) and laboratorial (hydrodistillation) methods by chemical class. Montenegro, RS, April 2017.

Chemical Class	Scarification (wt.%)	Hydrodistillation (wt.%)
Hydrocarbon monoterpenes	96.88	83.87
Alcohols	0.57	8.90
Aldehydes	0.52	0.45
Ketones	-	0.29
Esters	0.18	4.22
Hydrocarbon sesquiterpenes	1.00	0.33
Others	0.04	0.05

Although it presented a more diverse composition, the essential oil obtained by hydrodistillation had the lowest extraction yield, which was up to five times lower than that obtained by scarification. This may have occurred because whole fruits were used, as Frizzo et al. (2004) reported an average content of EO of 0.45 wt.% for fruits of the cultivars 'Caí' and 'Montenegrina' (*C. deliciosa*) cultivated in the same region of this study, also employing hydrodistillation, but using fresh fruit ground peels only.

Darjazi (2015), comparing the EO composition of 'Dancy' tangerine peel (*C. reticulata*) obtained by cold pressing and hydrodistillation, also observed important differences relative to the content of monoterpene alcohols and hydrocarbons. The author attributed the highest proportion of terpene alcohols in hydrodistillation to the hydrolysis of other components such as esters, which may react with water under high temperature (approx. 100 °C) to form alcohols and acids. The slightly lower content of monoterpene hydrocarbons in the EO obtained by this method can be explained by polymerization due to the acidification of cooking water during hydrodistillation (Darjazi, 2015).

According to Serafini et al. (2002) and Silveira et al. (2012), the fact that the raw material remains in direct contact with hot water for long periods of time in hydrodistillation may promote

the degradation of some compounds (especially the thermolabile ones). During hydrodistillation, hydrolysis, hydrosolubilization, or thermal degradation processes can occur, these being the main problems reported in this method and those responsible for reductions in the essential oil yield (Talati, 2017). Phandaripande and Makode (2012) pointed out that in the presence of small amounts of the organic acids during heating, gelatinization of suspended pectin and its heteropolysaccharides may occur. It is believed that the presence of this substance may also have negatively influenced the extraction yield, hindering the passage of water vapor containing EO, during the hydrodistillation of Citrus fruits.

Therefore, in view of the greater number of substances present in essential oils extracted by hydrodistillation in the present study, the greatest potential of this method is emphasized when the objective is the qualitative characteristics of the essential oil, rather than its yield. Obtaining essential oils with a more diverse composition has justified its importance when considering the numerous applications that these compounds can have, in food, pharmaceuticals, cosmetics, and perfumery industries to cleaning products, aromatherapy, pest control, and pathogen inhibition (Palazzolo et al., 2013). According to Rafiq et al. (2018) Citrus peel and bagasse is also a promising source of low-cost nutraceutical compounds for the food industry, for being rich in pectin, fibers, and polyphenols.

The higher yield observed in scarification method, up to five times higher than hydrodistillation, justifies its use on a large scale by the industry, and the average yield obtained (0.53 wt.%) was quite similar to the results reported by Frizzo et al. (2004), considering that this author tested this same method to obtain peel essential oil of green fruits of 'Caí' and 'Montenegrina' (*C. deliciosa*) (0.60 wt.%), grown in the same region, with the evaluations carried out by these authors occurring in a longer period - from March to June. However, it should be noted that the technical recommendation is that the hand thinning of *C. deliciosa* grown in Rio Grande do Sul to be carried out between the months of January and March, or until the fruits reach a maximum of 2.0 cm in diameter (2018). In this study, the first evaluations carried out coincided with the beginning of industrial activities, and it was precisely in the first half of March that the highest extraction yields were obtained in both methods. Thus, the period that provided the highest oil yield was the closest to that recommended for thinning by previous studies, and it is possible, in accordance with the existing technical information, to recommend that the removal of green fruits of *C. deliciosa* for the extraction of essential oil to be carried out at this time.

4 CONCLUSIONS

Based on the results, scarification provided essential oil yields up to five times greater than in hydrodistillation. However, the essential oil obtained by hydrodistillation had a greater diversity than scarification relative to the number of compounds detected, with the presence of methyl N-methylanthranilate and terpinen-4-ol among the major compounds, which were not detected in scarification. Considering essential oil production, scarification may be considered as the most suitable method, whereas hydrodistillation can be recommended when considering the essential oil composition, especially regarding the obtainment of terpene alcohols, ketones, and aldehydes, compounds which have an important influence on essential oil aroma and applicability on perfumery and cosmetics industries.

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