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Sea buckthorn (*Hippophae rhamnoides*) oil extracted with hexane, ethanol, diethyl ether and 2-MTHF at different temperatures – An individual assessment★,☆☆,☆

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ABSTRACT

Sea buckthorn oil (SBO) has been individually extracted using two green solvents (2-methyltetrahydrofuran (2-MTHF) and ethanol) and two conventional solvents (hexane and diethyl ether) using accelerated solvent extraction at four different temperatures (60, 90, 120 and 150 °C). The efficiency of the extraction was evaluated in terms of oil yield by weight difference, the quantification of α-tocopherol and β-carotene by HPLC and the evaluation of fatty acid profile by GC-FID/MS. The results were treated separately so any effect of the temperature was clearly seen for each solvent, and the fatty acid profile data was further treated jointly using a principal component analysis, as it is one of the most valued parts of sea buckthorn oil. All solvents revealed different optimal extraction temperature when in terms of oil yield; for ethanol was observed at 90 °C (21.75%), for hexane was at 60 °C (23.25%), for 2-MTHF was at 150 °C (14.65%) and for diethyl ether was at 120 °C (24.98%). The present work shows the optimal extraction temperature for SBO for each solvent studied depending on aim of the extraction.

1. Introduction

SBO can be extracted from the pulp and the peel or from the seeds. Both oils have been shown to have potential health benefits, including but not limited to improvements in blood lipid profile, cardioprotective properties and other antioxidant benefits (Guo et al., 2017; Olas, 2018). The most important bioactive components include palmitoleic acid and β-carotene in the berry oil and linolenic acid and α-tocopherol in the seed oil (Dulf, 2012). The unique nutritional profile of sea buckthorn oil makes it very valuable for the food and feed industry to use it as an ingredient in the formulation of diverse food products (Vilas-Franquesa et al., 2020).

Recent works on the extraction of SBO include the study of ultrasound-assisted extraction (Sanwal et al., 2022; Bhimjiyani et al., 2021), the study of supercritical and subcritical extraction technologies (Dienaite, Barauskiene, & Venskutonis, 2021; Zheng et al., 2017) and the study of solvent-free, microwave-assisted extraction (Périno-Issartier et al., 2011). The use of novel techniques in sea buckthorn oil extraction has been principally focusing on the extraction by non-polar techniques or even without the use of solvents. Nevertheless, the use of solvents still poses a great advantage, as it is a cheaper technique compared to the supercritical extraction, it can be combined with other extracting techniques such as microwave or ultrasound extraction, and the use of a solvent helps achieve great diffusivity and a great oil yield (Hrabovski et al., 2012). Moreover, solvent extraction is being adapted to the sustainable needs of the industry, attempting vegetable oil extractions with green solvents and more efficient techniques. Sea buckthorn berry oil has been recently extracted with ethanol and 2-MTHF using pressurized liquid extraction technique, achieving greater concentration of β-carotene in the extracted oil when compared to the oil extracted with hexane as conventional non-green solvent (Vilas-Franquesa et al., 2022). Nevertheless, the individual effect of

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green solvents has not been reported. In this line, more data should be collected to understand the behavior of the individual use of green and conventional solvents, on the extraction of sea buckthorn oil at different temperatures. The present experimental research was designed to fill that knowledge gap.

Understanding the individual effect of specific solvents – especially green solvents – on the extraction of oil from vegetable matrices is very important for its subsequent application in food industries and the change towards more sustainable extraction processes. Thereupon, the aim of the present work was to understand the nutritional composition of SBO individually extracted with ethanol and 2-MTHF as green solvents. Finally, as conventional solvents are still widely used in the recovery of bioactive compounds from vegetable matrices, hexane and diethyl ether have also been individually used to extract SBO from SB dried berries, and the nutritional quality of the outcoming oil has also been investigated. The nutritional quality was assessed by means of α-tocopherol and β-carotene concentration as well as the percentage of saturated, monounsaturated, and polyunsaturated fatty acids (SFA, MUFA and PUFA, respectively). To deeply understand the behavior of each of the solvents used on the extraction yield and recovery of bioactive compounds from SBO, a pressurized liquid extraction system and different extraction temperatures were used (60, 90, 120 and 150 ºC).

2. Experimental design

2.1. Solvents and material

Hexane, ethanol, diethyl ether and 2-methyltetrahydrofuran were used for the experiment. *n*-Hexane (with isomers) 99% purity (HPLC grade) was purchased from Labbox Labware, S. L., Catalunya, Spain. 2-Methyltetrahydrofuran (2-MTHF) stabilized with 2,6-di-tert-butyl-4-methylphenol was purchased from Merck KGaA, Darmstadt, Germany. Diethyl Ether, stabilized with 6 ppm of BHT and Ethanol absolute (99.8%) were purchased from Panreac Química S. A. U., Catalunya, Spain.

Polytetrafluoroethylene (PTFE) O-rings, PEEK seals, cell frites, 20 mm cellulose filters and PTFE-lined silicone septa for the ASE were purchased from Restek Corporation, Pennsylvania, U.S.

2.2. Sample preparation

A sack of sun-dried sea buckthorn berries weighing 15 kg was purchased from a local harvester from Romania. The cultivar is specifically located in the north-east region of Romania. The berries were categorized as the subspecies *caucasica*. Dried sea buckthorn berries were grinded down with a Thermomix® TM 21 (Vorwerk, Wuppertal, Germany). The particle size distribution of the powder was measured by gravimetry using sieves of different mesh sizes. Particle size distribution was quantified twice (by "Centro Nacional de Tecnologia Alimentaria" (CNTA, Navarra, Spain) and Office, S.L. (Barcelona, Spain)). Approximately 8 g of dried and ground sea buckthorn berries were mixed thoroughly with diatomaceous earth (DE) at a ratio of 4:1. An ASE extraction cell was filled with a cellulose membrane and the mix, in that order. The cell was closed and inserted in the ASE cell rack.

2.3. Oil extraction and yield

A total of four solvents and four temperatures were tested in the present research using ASE methodology, summing up a total of 16 experimental conditions with two independent variables. SBO was extracted from sea buckthorn dried berry powder by using an Accelerated Solvent Extractor 200 (Dionex, Thermo Fisher Scientific, California, U.S). The pressure was set at 1500 psi, static time at 10 min, preheating at 5 min, flushing volume at 30% of the total cell volume, purging time at 30 s and one extraction cycle. The temperature was set at 60, 90, 120 or 150 °C. The Soxhlet extraction was performed using a Soxhlet apparatus with the same amount of sample for a total of 5 h with hexane as extraction solvent.

After the extraction was finished, the extracted solution was poured into a spherical ball flask. The flask was then immediately attached to a rotavapor for 45 min to allow the solvent to evaporate at 45 °C and 150 mbar of pressure. The flask was then allowed to cool and subsequently weighed in an analytical balance for the yield. Immediately after, the oil was stored in amber tinted chromatography vials at − 80 °C for further analysis.

Ethanol and 2-MTHF dried extracts were further mixed with water (at room temperature) since during the extraction some polar compounds were dragged out, possibly derived from the physical characteristics of the used solvents (Vilas-Franquesa et al., 2022). The mixture of SBO extracted with ethanol and water resulted in a clear solubilization. The oil was recovered from the walls of the lab flask by dissolving it with hexane. Dissolution was complete and SBO was obtained after solvent drying at 45 ºC using a rotary evaporator. The mixture of SBO extracted with 2-MTHF and water resulted in a fuzzy mixture and therefore another separation strategy was used. The content of the lab-flask was poured into a centrifugal vial and submitted at 10,000 rpm for 10 min at room temperature. SBO was recovered from the upper phase using a glass Pasteur pipette. The extraction yield was measured by weight difference after the solvent containing the oil coming from the extraction was fully evaporated.

2.4. β-carotene and α-tocopherol analysis

A simultaneous quantification of β-carotene and α-tocopherol was adapted from Gimeno et al., (2000) and was performed as previously described (Vilas-Franquesa et al., 2022). DL-α-tocopherol acetate (HPLC standard, Merck KGaA, Darmstadt, Germany) was used as an internal standard, giving steady recovery values of 70%. α-tocopherol (synthetic, ≥96%, HPLC standard) and β-carotene (synthetic, ≥93%, analytical standard) from Merck KGaA (Darmstadt, Germany) were used as standard. Calibration curves for both analytes can be observed in the Supplementary Material.

2.5. Fatty acid profile

A rapid extraction methodology developed by Lamba, Modak, & Madras (2017) was adapted to sea buckthorn oil as previously described (Vilas-Franquesa et al., 2022). Peak identification was performed using three different techniques; (1) identification with a standard mix of alkanes, (2) using Kovats retention index and (3) GC-MS identification (GC System 7890 A attached to an MS triple-axis detector 5975 C (Agilent Technologies, California, U. S.)) with the Wiley library and comparison with the retention time of bought standards of methylated fatty acids (Supelco 37 Component FAME Mix, Merck KGaA, Darmstadt, Germany), as previously reported (Vilas-Franquesa et al., 2022).

2.6. Data analysis

All statistical analysis was performed with the software R-4.0. Assumptions were checked by first visually interpreting the Q-Q and boxplots from all analysis. Normality was double-checked by the Shapiro-Wilk test. One-way ANOVA was performed to each solvent's results including the final extraction yield, the concentration of the vitamers α-tocopherol and β-carotene, SFA, MUFA and PUFA to understand differences between temperatures in each single solvent. Further analysis involved the use of Tukey's *post hoc* tests to understand the source of the statistical significant difference.

Sea buckthorn dried berry is a very complex material to work with during oil extraction, especially when analyzing the fatty acid content, as the berry oil contains high amounts of palmitoleic and palmitic acids and the seed oil contains high amounts of oleic, linoleic and α-linolenic

acids. In the present experimental research, the fatty acid profile was analyzed by using the principal component analysis (PCA). The PCA is a useful technique when analyzing the fatty acid profile in different samples, as it allows to discriminate between samples using a two-dimensional graph through a dimension reduction of the variables. In the PCA analysis, an additional extraction with Soxhlet was run and included as reference method. Further analysis involved the use of fatty acid groups (SFA, MUFA and PUFA) and the individual assessment of each solvent on the extraction of the aforementioned compounds. All oil extractions and analyses were performed in triplicate.

3. Results and discussion

3.1. Extraction of SBO with hexane

Hexane has been previously reported as a temperature-dependent solvent. It has been shown to increase oil yield in the extraction of corn and oat oil (Moreau et al., 2003), amaranth seed oil (Kraujalis et al., 2013) and echium seed oil (Castejón et al., 2018). Nevertheless, the present experiment showed that there was no significant effect of the temperature on the extraction yield of SBO when using hexane as a solvent, F (3, 8) = 1.142, p = .389 (Table 1). In that line, the temperatures of 90 and 120 °C achieved a higher non-significant extraction yield when compared to the other two temperatures used, 90 °C being the most efficient.

In contrast, when using extraction temperatures of 60 °C and 90 °C the recovery of α-tocopherol from SBO using hexane was significantly greater when compared to higher temperatures (120 °C and 150 °C, F (3, 20) = 6.701, p < .05, Table 1). As reported earlier by Moreau et al. (2003), higher temperatures can achieve higher amounts of tocopherols using hexane as the extraction solvent. However, the original food matrix may play a role in the extraction of these non-polar compounds. Moreau et al. (2003) showed that, while the recovery of γ-tocopherol from corn extracts was higher at higher temperatures, the recovery of the same compound from oat extracts was lower at higher temperatures. The same authors explained however that the reported values were very similar and that increasing the extraction temperature did not yield a significant improvement on the recovery of γ-tocopherol. In the present work, results were significantly different depending on the temperature used when using hexane as extraction solvent. The recovery of α-tocopherol from SBO using hexane was higher at lower extraction temperatures (Table 1), making the extraction similar to that observed by Moreau et al. (2003) for oat extracts. Different food matrices imply that tocopherols may be found in different conformations, explaining the differences of tocopherol extraction at different temperatures (Marquardt et al., 2016). A more linear, saturated conformation would be more likely to be extracted by hexane rather than with other more polar solvents since this conformation would benefit from using a non-polar solvent for the extraction. In fact, hexane extracted more tocopherols from African breadfruit seed when compared to butanol or isopropanol extraction, two more polar solvents (Nwabueze and Okocha, 2008). In addition, as temperature rises the diffusivity of hexane in the sample increases as well (Perez et al., 2011) therefore suggesting a better extraction at higher temperatures. Nevertheless, here we show that at lower extraction temperatures, the best results of α-tocopherol were achieved. Likewise, the concentration of β-carotene in the extracted SBO was statistically significantly affected by changes in the extracting temperature when using hexane as extraction solvent, F (3, 20) = 23.055, p < .05 (Table 3). At 60 °C and 90 °C the recovery of β-carotene from SBO was significantly greater when compared to higher temperatures. No significant differences were found between the higher (120 and 150 ºC) nor the lower temperatures (60 and 90 ºC).

SBO extracted with hexane also gave significantly different percentages of fatty acids depending on the extraction temperature. Statistically different results were observed in the SFA distribution, F (3, 19) = 12.400, at p < .05 and in the MUFA distribution, F (3, 19) = 7.556, at p < .05. The percentage of PUFA in the resulting oil extracted with hexane was not affected by using different temperatures (Table 1). The recovery of MUFA and SFA followed an opposite pattern across all extractions. Using lower temperatures (60 and 90 ºC) during extraction resulted in an oil with a significantly greater percentage of SFA yet a lower percentage of MUFA when compared to the oil extracted at higher temperatures (120 and 150 ºC). Thus, the greater the temperature, the greater the concentration of MUFA in the resulting SBO and the lower the concentration of SFA. In contrast, Moreau et al. (2003) showed that lower temperatures of extraction (40 ºC) achieved greater percentages of free linoleic acid (included in the MUFA group herein) from corn samples when compared to higher temperatures (100 ºC). It should be noted that the lower temperatures in the present experiment are slightly higher than those used by Moreau et al. (2003) (60 ºC compared to 40 ºC). In addition, it could be seen that the results indicate a similar rising behavior at temperatures of 120 and 150 ºC.

The temperature dependency of hexane reported by other authors in terms of oil yield is not proven when extracting the oil from sea buckthorn berries. Nevertheless, there is a temperature-dependency for the extraction of α-tocopherol and β-carotene in the same matrix. This translates into an advantage when using hexane as solvent, since the extraction at lower temperatures (60 or 90 ºC) will recover high amounts of these bioactive compounds in expense of low quantity of energy (when compared to the extraction at higher temperatures). This is especially important when the extraction aims at the recovery of one of these bioactive compounds, such as is the production of oil supplements. Nonetheless, the extraction at 60 and 90 ºC also leads to an greater recovery of SFA and lower recovery of MUFA. Whereas the difference does not seem to be particularly great, it is significant and may limit the application of hexane for industrial purposes.

3.2. Extraction of SBO with ethanol

Ethanol has been extensively studied to recover certain bioactive compounds from vegetable matrices. For instance, the use of ethanol, or a mixture of ethanol and water have been studied on the extraction of oil from Echium seeds, showing promising results in the extraction yield and nutritional quality of the final oil (Castejón et al., 2018). In the

Table 1
Nutritional quality of SBO extracted by ASE using hexane at different temperatures.

	Dependent variable					
Temperature (ºC)	Yield	α-tocopherol	β-carotene	SFA	MUFA	PUFA
60	22.67 ± 0.28	0.934^{a} ± 0.058	1.363^{a} ± 0.060	37.412^{a} ± 1.471	46.073^{b} ± 1.434	15.611 ± 1.033
90	23.56 ± 0.48	0.920^{a} ± 0.045	1.339^{a} ± 0.036	37.180^{a} ± 0.721	46.157^{b} ± 0.878	15.767 ± 0.174
120	23.25 ± 0.18	0.842^{b} ± 0.051	1.131^{b} ± 0.128	35.561^{b} ± 0.461	47.928^{a} ± 0.364	15.572 ± 0.307
150	22.84 ± 0.65	0.843^{b} ± 0.051	1.077^{b} ± 0.022	35.617^{b} ± 1.202	47.717^{a} ± 1.651	15.639 ± 0.454

Yield expressed as g of SBO / 100 g of dried sea buckthorn berries; α-tocopherol and β-carotene content expressed as g / 100 g SBO; SFA, MUFA and PUFA values expressed as percentage of total fatty acids.
All values are expressed as mean ± SD
Different superscripts show significant differences at p < .05.

present research, the extraction yield was also significantly affected depending on the extraction temperature when extracting SBO with ethanol, F (3, 8) = 4.464, $p < .05$ (Table 2). The *post hoc* tests revealed that there were significant differences in the extraction yield of ethanol at 90 °C when compared to 120 °C or 150 °C using the same solvent, being lower in the latter two. The extraction at 90 °C yielded more oil than the extraction at 60 °C, although the difference was non-significant. Similarly, extracting corn and oat oil with ethanol at 100 °C also yielded more oil than at 40 °C, although this difference was significant (Moreau et al., 2003), probably derived from the higher difference in temperature. In addition, results from other authors indicated that the higher the extraction temperature, the higher the oil yield when using ethanol as the extracting agent (Castejón et al., 2018; Jablonsky et al., 2015). Nevertheless, the present experiment had the limitation of adding an extra step during ethanol extraction of SBO, therefore possibly compromising the final yield. Consideration should be taken to optimize the extraction of water-soluble compounds from SBO extracted with ethanol to see if this step could have been affecting the oil yield results.

Temperature significantly affected the concentration of α-tocopherol in SBO extracted with ethanol as well, F (3, 20) = 5.708, $p < .05$. At temperatures of 60 °C and 120 °C, the recovery of α-tocopherol from SBO was statistically significantly greater than extracting the oil at 90 °C (Table 2). High temperatures have not been used until the moment to determine the recovery of α-tocopherol from vegetable oils using ethanol. Some authors used lower temperatures (50 and 60 °C) to extract tocopherols from sunflower collets (Baümler et al., 2017), yet no clear difference was observed between both temperatures on the recovery of tocopherols. The approximate same pattern and same values were drawn from both extractions, also after increasing the extraction time. The previous year, Baümler et al. (2016) already investigated the differences in the recovery of tocopherols from sunflower oil after extraction with hexane and ethanol at two different temperatures (i.e. 50 and 60 ºC) and showed a higher recovery of tocopherols when extracting the oil at 60 °C. Thus, a slight increase in the extraction temperature resulted in a higher recovery of tocopherols from the oil when extracting it with ethanol. Nonetheless, different results have been observed in the present study. Higher temperatures (90, 120 and 150 ºC) decreased the concentration of α-tocopherol in the resulting oil when compared to the lower temperature used (60 ºC, Table 2). The second temperature applied was 90 ºC, involving a temperature rise of 30 ºC, which was the lower temperature jump when comparing the lowest temperature to any other extraction temperature. The difference of 30 ºC is far greater from what Baümler et al. (2016) studied and therefore it could explain part of the differences obtained herein. In general terms, extracting the oil at 60 °C led to a higher recovery of α-tocopherol than extracting at higher temperatures, although some temperatures may lead to non-significant differences (Table 2). The extraction at 90 °C resulted in the lowest amount of α-tocopherol, indicating that after the first drop in its concentration, increasing the temperature positively influenced the presence of α-tocopherol. Interestingly, no significant differences were observed on the concentration of α-tocopherol between the temperatures of 150 °C and 60 °C or 120 °C, showing that the presence of α-tocopherol was non-significantly different.

There was also a significant effect of the temperature on the concentration of β-carotene in SBO extracted with ethanol, F (3, 20) = 15.999, $p < .05$. The oil extracted at 120 °C achieved the greatest recovery values of β-carotene from SBO when compared to the oil extracted at any other temperature (Table 2). The difference was only significant when comparing the values obtained extracting the oil at 120 °C against the values from the oil extracted at 60 °C or 150 °C. The progressive observable increase in the concentration of β-carotene from 60 to 120 ºC dropped dramatically when extracting SBO at 150 ºC. The results showed a clear improved concentration of β-carotene when increasing the temperature except for the extraction at 150 °C, at which the concentration of β-carotene dropped significantly. This drop may be derived from the possible degradation of the analyte at higher temperatures and short time (Knockaert et al., 2012).

When analyzing the fatty acid profile, the ASE ethanolic extraction showed differences in the percentage of PUFA across the studied temperatures, F (3, 19) = 4.467, at $p < .05$. No significant differences were observed in the distribution of MUFA and SFA across temperatures in the ethanol-extracted SBO. SBO extracted with ethanol at 150 ºC yielded significantly more PUFA when compared to the oil extracted at 120 ºC (Table 2). The extraction at 150 ºC resulted in an extracted SBO with greater percentage of PUFA when compared to all other temperatures, which may derive from the decrease in polarity at higher temperatures (Lu et al., 2002). However, no differences were observed between other temperatures, meaning that the extraction at 120 ºC yielded the oil with the lowest percentage of PUFA and the extraction at 150 ºC yielded the higher percentage of the same group of fatty acids. This led to understanding that extractions using ethanol may lead to greater recovery of PUFA at lower and higher temperatures than 120 ºC, although more evidence should be brought on the ideal extraction temperature of PUFA from SBO using ethanol as extraction solvent.

The extraction with ethanol leads to the recovery of great amounts of β-carotene, especially greater when compared to hexane or other solvents, proving it useful for this purpose (Tables 1, 2; Vilas-Franquesa et al., 2022). Whereas the extraction with ethanol at 120 ºC is not the most efficient in terms of yield, it is the optimal extraction for β-carotene, and this could be interesting for its application in the food supplements or nutraceutical industry, where there concentration of bioactive compounds in the ingredients is key for their success. In addition, ethanol also emerges as a solvent to be used in the extraction of SB seed oil as well, as it can extract the highest amount of α-tocopherol at 60 ºC without significantly compromising the yield (Table 2).

3.3. Extraction of SBO with diethyl ether

Diethyl ether is a petroleum based solvent that has been also occasionally used in the extraction of vegetable oils, showing good recovery of the bioactive compounds present in the original matrix (Dey and Rathod, 2013). Diethyl ether was used in the present research because it has a lower boiling point when compared to hexane, and this could influence the nutritional quality or the yield of the final oil, as previously

Table 2
Nutritional quality of SBO extracted by ASE using ethanol at different temperatures.

	Dependent variable					
Temperature (ºC)	Yield	α-tocopherol	β-carotene	SFA	MUFA	PUFA
60	$20.96^{ab} \pm 0.82$	$0.945^{a} \pm 0.051$	$1.653^{b} \pm 0.054$	37.846 ± 0.929	44.263 ± 0.876	$12.512^{ab} \pm 0.216$
90	$21.75^{a} \pm 0.18$	$0.897^{b} \pm 0.007$	$1.698^{ab} \pm 0.050$	37.882 ± 1.357	45.516 ± 1.335	$12.414^{ab} \pm 0.322$
120	$20.09^{b} \pm 0.62$	$0.932^{a} \pm 0.022$	$1.768^{a} \pm 0.075$	37.030 ± 3.053	46.414 ± 2.391	$11.573^{b} \pm 1.038$
150	$20.15^{b} \pm 0.73$	$0.931^{ab} \pm 0.007$	$1.543^{c} \pm 0.049$	37.712 ± 1.908	45.175 ± 2.227	$12.907^{a} \pm 0.596$

Yield expressed as g of SBO / 100 g of dried sea buckthorn berries; α-tocopherol and β-carotene content expressed as g / 100 g SBO; SFA, MUFA and PUFA values expressed as percentage of total fatty acids.
All values are expressed as mean ± SD
Different superscripts show significant differences at $p < .05$.

shown (Juhaimi et al., 2019). It can be seen in Table 3 that there was a significant effect of the temperature on the extraction yield of SBO extracted with diethyl ether, $F(3, 8) = 8.251$, $p < .05$. The *post hoc* tests revealed that there was a significant difference between the extraction yield obtained at 120 °C when compared to the extraction yield obtained at 60 and 150 °C, being lower in the latter two. No significant differences were observed in oil yield extracted at 90 °C compared to that extracted at 120 °C, although the latter temperature achieved greater yield. The extraction at 150 °C seemed to be the less efficient extraction temperature in terms of yield (Table 3). Literature did not provide enough evidence on the variation in vegetable oil yield using diethyl ether as the extraction solvent. It seemed reasonable to conclude that the extraction with diethyl ether had an optimum range of temperature when extracting SBO, which was somewhere around 120 °C.

In addition, there was a significant effect of the temperature on the concentration of α-tocopherol in SBO extracted with diethyl ether, $F(3, 20) = 69.689$, $p < .05$. Significant differences were observed in the concentration of α-tocopherol in SBO extracted at 60 and 90 °C when compared to the oil extracted at 120 and 150 °C. Thus, the greater the extraction temperature, the greater the efficiency in recovering α-tocopherol. As temperature rises, the solvent viscosity and density decrease and solvent diffusivity increases, subsequently yielding greater mass transfer and therefore increased recovery of α-tocopherol (Dey and Rathod, 2013). There is a clear lack of publications to date studying the effect of temperature on the extraction of tocopherols using diethyl ether. The novel investigation with this solvent at different extraction temperatures brings evidence on the effect that the temperature may have upon the extraction of valuable compounds. It should be noted that the recovery of α-tocopherol was higher when using extreme temperatures, meaning that it was higher when using 60 °C (low extreme) rather than 90 °C, or using 150 °C (high extreme) rather than 120 °C.

Similarly, there was a significant effect of the temperature on the concentration of β-carotene in SBO extracted with diethyl ether, $F(3, 20) = 216.274$, $p < .05$. Significant differences were found between the concentration of β-carotene in SBO extracted at 60 and 90 °C when compared to the oil extracted at 120 and 150 °C. The greater the extraction temperature, the greater the efficiency in recovering β-carotene, except when comparing the extraction at 120 ºC against that at 150 ºC, being higher in the former (Table 3). The results of diethyl ether were clearly opposed to the overall results since at the highest temperatures (120 and 150 ºC) the extraction of β-carotene was proportionally more efficient when compared to the extraction at the same temperatures using other solvents. However, as already mentioned and as observed in the use of other solvents, the extraction at 150 °C led to a drop in β-carotene concentration when compared to the previous temperature (120 °C), clearly showing the temperature-dependency of this compound (Strati and Oreopoulou, 2011).

Diethyl ether was the only solvent yielding significantly different percentages in all the groups of analyzed fatty acids. Differences were observed in SFA, $F(3, 19) = 15.720$, in MUFA, $F(3, 19) = 22.520$ and in PUFA, $F(3, 19) = 9.350$, all of them at $p < .05$. SFA constituted a greater part of the total fatty acids when the extraction was performed at 90 ºC when compared to all other temperatures (Table 3). The obtained data pointed to a maximum at the extraction temperature of 90 ºC, and a subsequent decrease as extraction temperature rose. There were no statistically significant differences between the percentage of SFA in SBO extracted at 60 and 120 ºC. However, extraction at 150 ºC yielded an oil with significantly lower amounts of SFA when compared to all other temperatures. Likewise, the percentages of MUFA in SBO extracted with diethyl ether also led to one temperature achieving the highest values (150 ºC) when compared to all other temperatures, although the concentration was not positively associated with temperature. However, in our previous research the percentages of MUFA in extracted SBO followed a completely opposite pattern when compared to the extraction profile of SFA. In line with SFA concentration, the highest temperature was the worst when analyzing the percentage of PUFA in the extracted oil, yielding an oil with the lowest percentage of that fatty acid group. No differences were observed when comparing other temperatures of extraction. PUFA are more prone to be oxidized due to their high degree of unsaturation, and high temperatures may help oxidize the molecule and therefore to lose certain amounts (Fournier et al., 2006), at least when using diethyl ether as extraction solvent, as it is shown in the present experiment (Table 3).

Diethyl ether could be used for the extraction of both α-tocopherol and β-carotene at the specific temperature of 120 ºC achieving also the best process yield and lower amounts of SFA and high amounts of PUFA. This along with its boiling point (34.60 ºC) makes this solvent especially interesting. However, use of diethyl ether would be limited to the cases in which subsequent formulation would only require the use of this solvent, as it is the solvent achieving lower concentration of both bioactive compounds in relation to the other solvents (Vilas-Franquesa et al., 2022). Nevertheless, in cases where yield is the most important parameters this solvent is a good choice. Lastly, it could be used for the extraction of MUFA (especially in berry oil where palmitoleic acid is more concentrated) at 150 ºC without compromising the content of α-tocopherol.

3.4. Extraction of SBO with 2-MTHF

2-MTHF is a solvent that is recently gaining interest in the solvent extraction industry, as it is a solvent that is produced from biomass and it has been produced for several years (Eldeeb and Akih-Kumgeh, 2018). 2-MTHF is also considered a green solvent and had been performed well on vegetable oil extractions in the past when compared to conventional solvents (Bourgou et al., 2019; Rebey et al., 2019). In fact, in the present research a significant effect of the temperature on the extraction yield in SBO extracted with 2-MTHF has been observed, $F(3, 8) = 75.005$, $p < .05$ (Table 4). Tukey's *post hoc* test revealed statistically significant differences in the yield of all extraction temperatures. The greater extraction yield was achieved at 150 °C, and in a decreasing order at 120 °C, 90 °C and 60 °C. The difference between the latter and the former was more than 2%. The results showed this solvent to be clearly dependent on temperature changes. The extraction of oil was positively associated with temperature. Results from other scientific publications

Table 3
Nutritional quality of SBO extracted by ASE using diethyl ether at different temperatures.

	Dependent variable					
Temperature (ºC)	Yield	α-tocopherol	β-carotene	SFA	MUFA	PUFA
60	$24.21^{b} \pm 0.50$	$0.613^{b} \pm 0.020$	$0.267^{c} \pm 0.013$	$36.320^{b} \pm 0.699$	$45.303^{b} \pm 0.688$	$17.181^{a} \pm 0.203$
90	$24.52^{ab} \pm 0.20$	$0.562^{b} \pm 0.034$	$0.244^{c} \pm 0.037$	$37.160^{a} \pm 1.590$	$44.440^{c} \pm 1.424$	$17.356^{a} \pm 0.549$
120	$24.98^{a} \pm 0.02$	$0.787^{a} \pm 0.057$	$0.686^{a} \pm 0.025$	$36.156^{b} \pm 0.241$	$45.776^{b} \pm 0.373$	$17.158^{a} \pm 0.094$
150	$23.92^{b} \pm 0.13$	$0.820^{a} \pm 0.027$	$0.641^{b} \pm 0.026$	$35.283^{c} \pm 0.201$	$47.036^{a} \pm 0.310$	$16.859^{b} \pm 0.091$

Yield expressed as g of SBO / 100 g of dried sea buckthorn berries; α-tocopherol and β-carotene content expressed as g / 100 g SBO; SFA, MUFA and PUFA values expressed as percentage of total fatty acids.
All values are expressed as mean ± SD
Different superscripts show significant differences at $p < .05$.

Table 4
Nutritional quality of SBO extracted by ASE using 2-MTHF at different temperatures.

	Dependent variable					
Temperature (ºC)	Yield	α-tocopherol	β-carotene	SFA	MUFA	PUFA
60	$11.960^{d} \pm 0.16$	$0.684^{ab} \pm 0.660$	$1.017^{a} \pm 0.016$	$38.919^{a} \pm 0.132$	45.281 ± 0.585	$14.117^{b} \pm 0.676$
90	$12.84^{c} \pm 0.15$	$0.715^{a} \pm 0.041$	$1.014^{a} \pm 0.061$	$37.429^{bc} \pm 0.942$	44.655 ± 1.384	$15.910^{a} \pm 0.352$
120	$13.85^{b} \pm 0.19$	$0.658^{ab} \pm 0.070$	$0.796^{b} \pm 0.062$	$37.881^{b} \pm 0.771$	45.511 ± 0.928	$14.829^{c} \pm 0.471$
150	$14.65^{a} \pm 0.37$	$0.620^{b} \pm 0.041$	$0.706^{b} \pm 0.071$	$37.011^{c} \pm 0.753$	45.607 ± 0.907	$15.722^{a} \pm 0.403$

Yield expressed as g of SBO / 100 g of dried sea buckthorn berries; α-tocopherol and β-carotene content expressed as g / 100 g SBO; SFA, MUFA and PUFA values expressed as percentage of total fatty acids.
All values are expressed as mean ± SD
Different superscripts show significant differences at $p < .05$.

used only one temperature, most of them performing extractions with 2-MTHF using a Soxhlet set-up (Bourgou et al., 2019; Rebey et al., 2019; Sicaire et al., 2015). Interestingly, 2-MTHF was used to extract limonene from orange peel at different times (30, 60, 90, 120, 150 and 180 min) and temperatures (30, 50, 70 and 90 °C) and found an increasing trend in the limonene yield when increasing either the extraction time or temperature (Ozturk et al., 2019). The limonene recovery yield jumped from around 0.5% at 30 °C to almost 1.5% at 70 °C, with a slight decrease when the temperature rose to 90 °C. The increasing trend in SBO extraction yield was also observed in the present experiment.

The behavior of 2-MTHF was expected to be similar to that of ethanol, according to polarity. However, the behavior of 2-MTHF was closer to that of diethyl ether. When investigating the effect of temperature on the recovery of α-tocopherol, a significant effect of the temperature on the concentration of α-tocopherol in SBO extracted with 2-MTHF was spotted, F (3, 20) = 3.107, $p < .05$. Tukey's *post hoc* test highlighted statistically significant differences in the concentration extracted at 90 °C when compared to the extraction at 150 °C, being higher in the former (Table 4). The temperature did not negatively affect oil yield – it increased – but it negatively affected oil composition, yielding lower amounts of α-tocopherol at higher temperatures when compared to lower temperatures. The results were also in line with what was observed in the extractions of SBO using hexane, also decreasing the nutritional quality of the oil as the extraction temperature rose. This could derive from the similar technical properties between hexane and 2-MTHF (Sicaire et al., 2015). The recovery of α-tocopherol was lower when extracting at 60 ºC when compared to 90 °C, but slightly higher than in the oil obtained at 120 °C, clearly showing the temperature-dependency for the extraction of compounds when using 2-MTHF (Ozturk et al., 2019).

Furthermore, there was a significant effect of the temperature on the concentration of recovering β-carotene in SBO extracted with 2-MTHF, F (3, 20) = 46.086, $p < .05$. Statistically significant differences were spotted in recovering β-carotene from SBO at 60 and 90 °C when compared to the extraction at 120 and 150 °C, being higher in the former temperatures (Table 4). In the case of β-carotene concentration, the greater the temperature used in the extraction, the lower the concentration of the analyte in the extracted SBO. Although the differences were non-significant, the extraction at 120 °C achieved greater concentrations of β-carotene in SBO when compared to the extraction at 150 °C. These results were in accordance with all other solvents, suggesting that the drop in the recovery of β-carotene at 150 ºC was indeed more subject to temperature change rather than to solvent choice. It was interesting to note when using 2-MTHF that the oil yield was negatively associated with the β-carotene concentration. In other words, at higher temperatures the extraction yield improved (Table 4) in detriment to the recovery of β-carotene (Table 4).

Extractions using 2-MTHF yielded significantly different percentages of SFA, F (3, 19) = 9.514, and PUFA, F (3, 19) = 17.110, both at $p < .05$. No significant differences were observed between the percentages of MUFA in the oil extracted with 2-MTHF when comparing different temperatures. The greater percentage of SFA in the oil extracted with 2-MTHF was obtained at 60 ºC, meaning that higher temperatures could lead to lower extraction of SFA and therefore, lower presence in the oil. In fact, the extraction at the highest temperature (150 ºC) resulted in an oil with a lower percentage of SFA. Although the difference was sometimes non-significant, the behavior of all the solvents showed a slight decrease in the percentage of SFA at the highest temperature. In addition, like what was observed with ethanol, the highest temperature yielded significantly higher percentages of PUFA when compared to the extraction at 120 ºC, but similar amounts when compared to the extraction at 90 ºC. Therefore, results could indicate a possible drop in the recovery of PUFA in SBO by polar solvents at some temperature around 120 ºC. However, this should be further investigated to add more evidence on the field. It was however clear that the highest extraction temperature did not achieve the poorest extraction of PUFA either using ethanol or 2-MTHF as the extraction solvents, suggesting the adequacy of the theoretical approach of the decrease in polarity of the most polar solvents at high temperatures (Lu et al., 2002).

The dependent variable that limits the use of 2-MTHF is the yield, which is strongly dependent on temperature. The yield increases almost 20% when comparing the extraction at 60 ºC against the extraction at 150 ºC, being higher in the latter (Table 4). This limits the use of 2-MTHF, which gains interest in the recovery of valuable ingredients instead of high volumes of product (i.e. nutraceutical, pharmaceutical industries). The most interesting extraction for this solvent is at 90 ºC, as it is the best extraction temperature for the recovery of α-tocopherol, β-carotene and PUFA and the extraction yield is only 12% lower when compared to the values obtained at 150 ºC (Table 4). Another interesting temperature of application is at 150 ºC, as it gives the best process yield with the greatest recovery of PUFA and great recoveries of α-tocopherol. The temperature of 150 ºC could be applied to the extraction of sea buckthorn seed oil.

3.5. PCA of fatty acids in SBO

A principal component analysis (PCA) was conducted on the six (6) most relevant fatty acids in sea buckthorn berry and seed oil with no rotation applied (namely palmitic, palmitoleic, stearic, oleic, linoleic and α-linoleic acids). The Kaiser-Meyer-Olkin (KMO) measure verified the sampling adequacy for the analysis. Bartlett's test of sphericity indicated that correlations between items were sufficiently large for PCA. An initial analysis was run to obtain eigenvalues for each of the components in the data. Two of the components showed eigenvalues over Kaiser's criterion of 1 and in combination explained 85.91% of the variance (Table 5). The scree plot confirmed the first two components to be the most relevant for explaining the variance of the statistical model. Therefore, the first two components were retained for the final analysis. No rotation was applied since the first two principal components showed a great fit with the raw data. The items that clustered on the first principal component were palmitic, palmitoleic, oleic and stearic fatty acids. The items that clustered on the second were linolenic and α-linolenic fatty acids. This was interesting, since the dimensions seemed to account for the saturated and mono-unsaturated fatty acids for the first principal

Table 5
Principal components and their respective eigenvalue and variance explained by the model. Eigenvalues greater than 1 were used to draw the PCA, according to Kaiser's criterion.

Dimension	Eigenvalue	Variance explained (%)	Variance explained (%, cumulative)
1	3.78	63.05	63.05
2	1.37	22.87	85.92
3	0.58	9.66	95.58
4	0.15	2.56	98.14
5	0.09	1.50	99.64
6	0.02	0.36	100.00

component and the poly-unsaturated fatty acids for the second principal component (Table 6).

The clustering on PCA was performed on the two main extracted principal components (PC1 and PC2) and the two independent factors (the solvent used and the temperature). The PCA main graph shows results from individuals in a scattered plot with PC1 in the X-axis and PC2 in the Y-axis. Individuals are plotted in the same cluster depending on the solvent used during the analysis, to investigate differences between solvents. Fig. 1 shows a clear difference using ASE or using Soxhlet as a technique to extract fatty acids from SBO if we compare the groups "Hexane" – extracted using hexane and ASE – against the "Control" group – extracted with the same solvent using the Soxhlet technique. According to the results from PCA, the extraction using Soxhlet achieved a greater extraction of the components building up PC1, those being oleic, stearic, palmitic and palmitoleic fatty acids, whereas the ASE extraction did not achieve great concentrations of those fatty acids. However, ASE extraction did achieve larger concentrations of the polyunsaturated fatty acids (PC2).

Looking at the main PCA, it was clear that the oil extracted with different solvents showed different fatty acid profiles. Specifically, there seemed to be a clear difference in the oils obtained by using diethyl ether, ethanol and hexane. However, the oil from the extractions using 2-MTHF did not separate in a new, isolated cluster. Instead, the cluster containing all the individual extractions with 2-MTHF was mixed up with all other clusters from the individual extractions using all other solvents (Fig. 1). The solvent 2-MTHF seemed to behave both as the most polar (ethanol) and the most non-polar solvents (hexane, diethyl ether). Interestingly, the overall average extraction with 2-MTHF resulted in an oil with a greater concentration of poly-unsaturated fatty acids (linoleic and α-linolenic fatty acids) when compared to the ethanol and hexane extractions. Although in a non-significant manner, a higher extraction of polyunsaturated fatty acids was reported by Sicaire et al. (2015) on rapeseed oil when using 2-MTHF for the extraction and comparing the results to other solvents'. The extraction with 2-MTHF achieved, on average, higher concentrations of saturated and mono-unsaturated fatty acids when compared to the extractions using hexane. The oil extracted with 2-MTHF contained lower amounts of poly-unsaturated fatty acids when compared to the extraction using diethyl ether, and similar concentrations of saturated and mono-unsaturated fatty acids.

Table 6
Contribution of every variable analyzed (fatty acid) to Dimension 1 and Dimension 2 of the PC model.

Variable analyzed	Contribution to Dimension 1 (%)	Contribution to Dimension 2 (%)
C16:0	23.355	0.004
C16:1	25.107	0.522
C18:0	23.714	2.235
C18:1	25.301	0.588
C18:2	0.683	50.448
C18:3	1.841	46.203

C16:0: Palmitic acid; C16:1: Palmitoleic acid; C18:0: Stearic acid; C18:1: Oleic acid; C18:2: Linoleic acid; C18:3: α-Linolenic acid.

The most polar solvent, ethanol, appeared in the main PCA (Fig. 1) as a more clearly isolated cluster. The most relevant difference relied on the extraction of fatty acids from PC2, which was on average higher when the oil was extracted using hexane or diethyl ether. Results however showed a possible slightly higher concentration of poly-unsaturated fatty acids in SBO extracted with ethanol when compared to the extraction with Soxhlet, as other authors have previously reported (Castejón et al., 2018). Contrarily to what observed by Pieber et al. (2012), pressurized liquid extraction using ethanol led to higher amounts of saturated and mono-unsaturated fatty acids (PC1) and lower amounts of poly-unsaturated fatty acids (PC2). Diethyl ether was the solvent that, in all the performed extractions, achieved a higher amount of poly-unsaturated fatty acids in the resulting oil (PC2). Compared to hexane, the extraction with diethyl ether was expected to achieve higher amounts of poly-unsaturated fatty acids due to the slightly more polar nature of the solvent (Freed et al., 1990).

Contrarily, temperature did not have a significant effect on the concentration of fatty acids on the resulting oil (Fig. 2). Therefore, the most important factor to consider in the extraction of fatty acids from SBO is the solvent rather than the temperature when using pressurized liquid extractions. There was a clearly separated cluster from the extraction using Soxhlet (Fig. 2). Thus, control samples showed clearly higher amounts of saturated and poly-unsaturated fatty acids presents in SBO when compared to ASE.

3.6. *Considerations for the applicability of the results*

The application of each solvent strongly depends on the ultimate outcome of the extraction. If the interest remains on obtaining a specific compound from SBO, the choice is the solvent that recovers the most quantity of the specific compound. For instance, ethanol would be the solvent of choice for β-carotene or α-tocopherol extraction, and hexane for MUFA and PUFA extraction, as we showed in our previous work (Vilas-Franquesa et al., 2022). If the interest remains in the most efficient solvent for yield extraction diethyl ether or hexane are the solvents of choice. Nevertheless, those are petroleum-based solvent and their production and use is not sustainable. In addition, there are specific production processes that may need the use of a specific solvent. For instance, ethanol is generally used as green solvent for the extraction of polyphenols from vegetable matrices, and the combination of ethanolic extracts is not uncommon. Therefore, for this specific purpose, ethanol could be used for the extraction and recovery of β-carotene and α-tocopherol and in that way obtain a product which could be subject to combination with other ethanolic extracts. However, after understanding which solvent is the best for the purpose of the extraction there is the need of understanding at which temperature this extraction should be performed. The present research gives insight on this by providing empirical data of the application of different temperatures when extracting SBO using hexane, diethyl ether, ethanol or 2-MTHF. This leads to the understanding of its possible application in the food, nutraceutical or pharmaceutical industries.

4. Conclusions

The best yield for the extraction of SBO with ethanol or hexane was achieved at 90 °C, and when using 2-MTHF the best result was achieved at 150 °C, whereas the best yield for the extraction of SBO using diehtyl ether was at 120 °C. Similarly, the best yield was obtained with diethyl ether at 120 °C. In addition, the extraction of SBO with 2-MTHF at 150 °C achieved the lower amounts of SFA and the greatest amounts of PUFA when compared to all other extractions with 2-MTHF. Extracting the oil with ethanol at 90 °C also achieved good values of PUFA.

The performed PCA on the fatty acid profile revealed that there was no clustering difference when extracting sea buckthorn oil at different temperatures, yet differences were clearly spotted when comparing different solvents. In that issue, diethyl ether showed greater

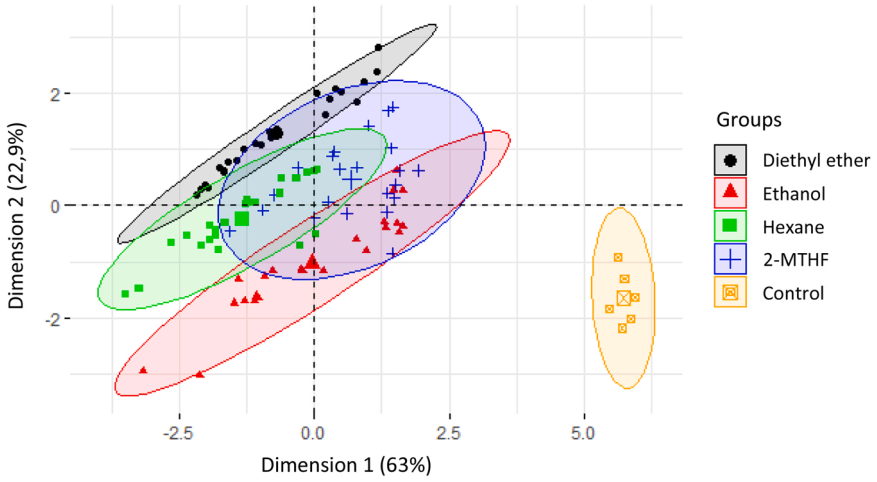

Fig. 1. Mapping of the samples in two different dimensions. Samples were grouped according to the solvent used during the ASE extraction, and the control (Soxhlet).

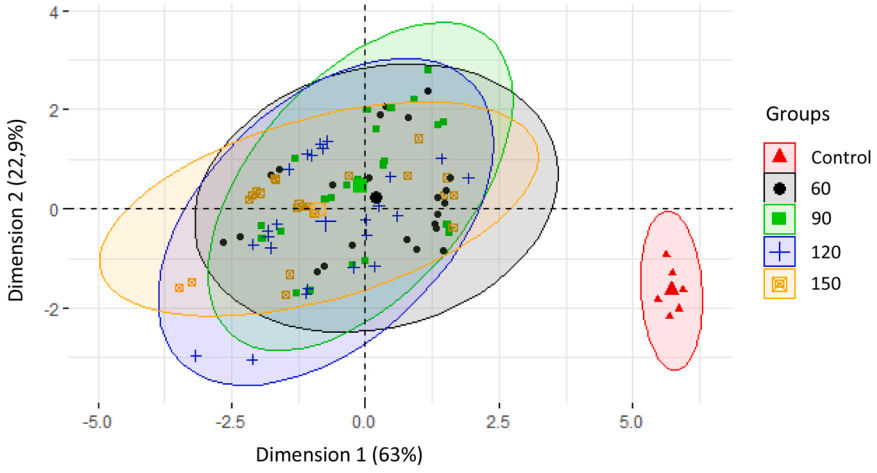

Fig. 2. Mapping of the samples in two different dimensions. Samples were grouped according to the temperature used during the ASE extraction, and the Control (Soxhlet).

concentration of PUFA whereas the extraction with ethanol led to the highest concentration of MUFA and SFA.

CRediT authorship contribution statement

Vilas-Franquesa: Investigation, Conceptualization, Methodology, Data curation, Writing, Editing. **Juan and Saldo**: Review, Editing, Validation.

Declaration of Competing Interest

The authors declare that there is no conflict of interest for the present work.

Data availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.jfca.2022.104752.

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