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Valorization of Sour Cherry and Cherry Seeds: Cold Press Oil Production and Characterization

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Abstract

The aim of this study was to produce cold press oils from sour cherry and cherry kernels and to characterize the oils for possible edible and non-edible usages. The oil yield was 55.9% and 51.3% with cold pressing, respectively. Although common oil physico-chemical properties were in accordance, their peroxide values were higher. Further, oil thermal properties, fatty acids, sterols and tocopherols compositions were determined. A total of 20 different volatile compounds were quantified in both samples. Both oil samples were described sensorially with 8 definition terms by the panel. Also, a consumer hedonic test was completed. Results indicated that although both oils are nutritious samples, their oxidation status was exceeding the limit value. Cherry syrup, astringent, and menthol were detected as negative sensory attributes. Consumer test scores indicated a neutrality for their appearance, aroma and flavor attributes. Overall, these cold press oils evaluated as not proper for direct edible consumption, but could be used in nutraceuticals, cosmetics and for energy generation purposes.

Keywords: sour cherry seed; cherry seed; cold press; oil; characterization; sensory

1. Introduction

Cherry fruits are botanically within the *Rosaceae* family, *Prunus* genus and *Cerasus* subgenus, which is distinguished by having the flowers in small corymbs of several together. The most commonly cultivated species are sour cherry (*Prunus cerasus*) and sweet cherry or cherry (*Prunus avium*). Their trees can grow up to 3-10 m and has twiggy branches. The plants are native to the temperate regions of the Northern Hemisphere. Sour cherry fruits are more sour and smaller than cherry fruits. Both fruits include approximately 82% water, 16% carbohydrate, 1% protein, and important amounts of vitamin C (12% of RDA) and vitamin A (8% of RDA), and some dietary fiber. Usually, they are consumed as fresh fruits, but also processed to their juices and concentrates, jams and jellies, and others [1, 2].

According to 2014 statistics, Turkey is the first producer of cherry fruit with 445.556 tons production, and third for sour cherry with 182,577 tons production [1].

It was stated that 55.000 tons of sour cherry were processed for juice, and 12.500 tons of sour cherry were processed for fruit puree in Turkey in the same year [3]. Since around 15% of fresh fruit is the seed, approximately 10.000 ton of sour cherry seeds were generated as waste. Cherry is usually consumed as fresh fruit, but a small portion of it was processed for jam and jelly type products. Their production statistics are not published, but a much lesser amount of cherry seeds were generated.

Valorization of agro-food processing by-products and wastes became a necessity for sustainable food production [4, 5]. One way of waste seed and kernel valorization is the production of cold pressed oils, if the material contains enough amounts of oil. In our laboratory, capia pepper seeds [6], tomato seeds [7], and grapefruit seeds [8] were valorized through cold press oil production. It was also stated that cold pressing is a green process which not requires oil refining, and yields very healthy and aromatic edible and/or non-edible oils which have been used

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by food, nutraceutical, pharmaceutic and cosmetic sectors [6, 8].

In literature, there are some limited number of studies with mostly solvent extracted sour cherry and cherry seed oils for their main components analysis [9-17]. In none of these studies, volatile compositions, thermal properties, sensory analysis and consumer tests were performed. Further, cold press production parameters were not studied. Therefore, it was worth to study cold press production of sour cherry and cherry seed oils, and to characterize the oils in detail.

The objectives of this study were to produce cold pressed oils from waste seeds of sour cherry and cherry fruits, and to fully characterize the cold press produced oils for possible uses through detailed physico-chemical, compositional and sensory analyses. The information generated in this study may help to valorize these waste seeds for cold press oil production and to develop new applications of the oils.

2. Materials and Methods

2.1. Materials

The sour cherry and cherry seeds (15 kg each) were provided by Dimes Fruit Juice Factory (Dimes Co., Tokat, Turkey) in 2016 processing season. The seeds were washed, drained and dried at room temperature. To separate the fruit kernels from seed shell, the stone seeds were broken down with a Jaw Crusher (Jeotest Co., Ankara, Turkey), and then the kernels were separated out by hand picking. The seed kernels were kept in deep-freezer at – 18 ^{o}C during the study. The seeds and their kernels are shown in Figure 1. All standards, solvents and chemicals were of analytical grade and purchased from Sigma (St. Louis, MO, US) or Merck (Darmstadt, Germany).

2.2. Seed and Kernel Analyses

The instrumental color values of the sour cherry and cherry seeds and their kernels were measured with a Minolta Colorimeter (CR-400, Osaka, Japan). Seed dimensions were determined with a digital caliper (CD-15CP, Mitutoyo Ltd., Andover, UK). The 1000-seeds weight was determined by weighing randomly selected 10 seeds (Sartorius ED224S, Sartorius, Germany) and multiplying with 100. Several seeds were broken with hand hammer, and the kernels and shells were separated and weighed to determine the meal: shell ratio. All measurements were replicated at least three times.

The proximate composition analysis of the kernels was also completed. Kernel moisture (%) contents with Ohaus MB45 moisture analyzer (Ohaus, Pine Brook, US) and water activity (aw) with the AquaLab 4TE water activity meter (Decagon Inc. US) were measured. The crude oil, crude protein and total ash contents of the kernels were measured by AOAC method 920.39, by the Kjeldahl of AOCS method Aa 5-38 and by AOCS method Ba 5a-49, respectively [18, 19].

2.3. Cold Pressing of the Kernels

Since the initial moisture contents (around 12-13%) of the kernels were appropriate for cold pressing, no drying or pre-roasting applied. The kernels were directly cold pressed with a laboratory scale single head, 1.5 kW power, 12 kg seed/h capacity cold press machine (Koçmaksan, ESM 3710, İzmir, Turkey). The operating conditions were as follows; 20 rpm screw rotation speed, 14 mm exit die and 45 ^{o}C oil exit temperature. Then, the oils were centrifuged (Sigma 2-16 K, Postfach, Germany) at 6797 g and filtered through Whatman no.1 paper (11 micron) to remove foreign materials. Finally, they were placed in amber colored glasses, flushed with nitrogen and stored in a fridge until further analyses.

The cold press oil yield was calculated following the equation given below;

Oil yield (%) = (A / B) * 100

A = amount of oil obtained by cold pressing (g)

B = total oil content (g) of the kernels determined by the Soxhlet technique

2.4. Physico-Chemical Properties of the Oils

Specific gravity with oil pycnometer by AOCS method Cc 10c-95 at 25 ^{o}C [19]; specific extinctions with a spectrophotometer (Shimadzu UV-1800, Shimadzu Co., Japan) by AOCS method Ch 5-91 [19]; refractive index with Abbe 5 (Bellingham and Stanley, UK) refractometer, and viscosity with Brookfield Viscometer (model DV II+Pro with Rheocalc software, Brookfield Eng. Lab., Inc., MA, USA) equipped with LV-SC4-18 spindle at 30 rpm at 25 ^{o}C were measured. Oil color values (L, a* and b*) were determined with a Minolta Colorimeter CR-400 (Minolta Camera Co., Osaka, Japan).

The free fatty acid contents and acid values of the oils were determined by the AOCS methods of Ca 5a-40 and Cd 3d-63 [19]. Oil peroxide values, *p*-anisidine values, iodine numbers, and saponification numbers were measured by the AOCS methods of Cd 8-53, Cd 18-90, Cd 1-25, and Tl 1a-64, respectively [19]. The oil unsaponifiable matters were measured by ISO 3596 method [20]. Total phenolics contents were measured by Folin-Ciocalteu reagent, and antioxidant capacities were estimated by the Trolox equivalent antioxidant capacity (TEAC) technique according to our previous study [21].

2.5. Thermal Properties of the Oils

Melting and crystallization temperatures and enthalpies of the oils were determined with a Perkin-Elmer 4000 Series Differential Scanning Calorimeter-DSC (Groningen, The Netherlands). Around 5-10 g sample was weighed and sealed in aluminium pans, and analyzed under 50 ml/min nitrogen flow rate with the following temperature program: heat from room temperature to 110 ºC by 10 ºC/min rate, then cool to -70 ºC by 10 ºC/min rate and hold at that temperature for 3 min for full crystal formation, and finally heat sample again to 50 ºC by 5 ºC/min rate. The Pyris 1 manager software was used to calculate the thermal parameters [6].

The oxidation induction times (OIT) were also measured with the DSC in the sealed pans by first heating from 30 ºC to 130 ºC at 20 ºC /min rate under constant nitrogen flushing (50 ml/min), and then an isothermal temperature programming at 130 °C with 50 ml/min purified oxygen (99.8%) was applied [8].

2.6. Fatty Acid, Sterol and Tocopherol Analyses of the Oils

The fatty acid methyl esters were prepared according to AOCS method Ce 2-66 and analyzed by gas chromatograph according to AOCS method Ce 1h-05 [19]. The GC was Agilent 7890B (Agilent Technologies, Palo Alto, CA, USA) donated with flame ionization detector (FID) (Agilent Technologies, Palo Alto, CA, USA), and HP 88 capillary column (100 m×0.25mmID×0.2µm film thickness, J&W Scientific Co, CA, USA). The analysis condition was as follows: oven temperature, 120 °C for 1 min, 175 °C (10°C/min) for 10 min, 210 °C (5°C/min) for 5 min and 230 °C (5°C/min) for 5 min; injection volume 1 µL, injector split ratio 1:50, flow rate 2 ml/min, hydrogen as carrier gas, injector and the detector temperatures were 250 and 280 °C. Fatty acid methyl esters were quantified by co-chromatography with FAME mixture standards (37-components, C4-C24, Supelco, Bellefonte, PA, USA).

The sterol composition of the oils was determined following the ISO 12228 method [22]. After separating sterol fraction on TLC, the analysis was completed with the same GC and DB5 capillary column (30 m × 0.25mm ID × 0.1 µm film thickness, J &W Scientific Co, CA, USA). The analysis program was as follows: oven temperature, 60 °C for 2 min, 60-220 °C (40°C/min) for 1 min, 220-310 °C (5°C/min) for 30 min; injection volume 1 µL, injector split ratio 1:100, flow rate 0.8 ml/min, hydrogen carrier gas (30 ml/min), injector and the detector temperatures of 290 and 300 °C, respectively. Commercially available standards (cholesterol, brassicasterol, stigmasterol, ß-sitosterol) were used under the same conditions to identify and quantify the sterols in the samples.

The tocopherol contents of the samples were measured with reverse-phase HPLC (Shimadzu Corporation, Kyoto, Japan) equipped with LC-20AT HPLC pump, DGU-20A5R degasser, CTQ-10ASVP column oven, and RF-20A diode array detector. The method of Grilo Câmara et al. was followed [23]. Briefly, 20 µl of samples (0.15 g oil in 3 ml dichloromethane) were injected by an autosampler (SIL-20AHT) into the Inertsil ODS-3 column (250mm x 4.6mm x 5µm, GL Sciences Inc., Japan). The elution flow rate was 1.6 ml/min isocratic, and methanol: water (98:2 v/v) was the mobile phase. The excitation and emission wavelengths of the detector were 290 and 330 nm. Quantification was performed using commercial tocopherol standards (Merck, Darmstadt, Germany).

2.7. Volatile Analysis of the Oils

Volatile compounds of the oil samples were analyzed following Krist et al. [24] and Yilmaz et al. [6]. Around 5 g oil, 1 g NaCI and 20 µl internal standard (1 µl of 2-methyl-3-heptanone dissolved in 10 ml methanol) were placed into an amber colored vial and vortexed for 1 min. The vial was kept at 50 °C for 15 min in a water bath, before immersing an SPME fiber (2 cm, 50/30 µm DVB/Carboxen/PDMS, Supelco, Bellafonte) into the vial headspace. Then, it was kept at 50 °C for another 45 min. Finally, fiber collected volatiles

were analyzed with GC/MS (Agilent 6890HB/Agilent 5875C mass spectrometer; Agilent Technologies, Wilmington, DE, USA) equipped with HP5 MS column (30 m × 0.25 mm, i.d. 0.25-µm film thickness, J & W Scientific, Folsom, CA, USA). The analysis was done under 1.2 ml/min flow rate of helium as a carrier gas with 1:2 split ratio. The temperature program was as follows; waiting at 40 °C for 1 min, heating to 200 °C (4 °C/min), heating to 230 °C (7 °C/min) and waiting at that temperature for 15 min. The working conditions of MS detector were 280 °C capillary direct interface temperature, 70 eV ionization energy, 35-350 amu mass range, 4.45 scans/sec scanning rate. National Institute of Standards and Technology and Wiley Registry of Mass Spectral Data were used for identification of compounds. Quantified of the identified volatiles was completed by comparing the peak area of 2-methyl-3-heptanone, internal standard. Quantification of all volatile compounds was based on the relative abundances calculated by the equation given below.

Mean relative abundance ((µg/kg) = [concentration of IS] x [peak area of compound] / [peak area of the IS]

2.8. Sensory Analyses of the Oils

The Quantitative Descriptive Analysis (QDA) was used following the methods given in Meilgaard et. al. [25]. There were 13 panelists (7 female and 6 male, aged between 21-48) and trained at least 15 hours in different days and sessions under the control of the panel moderator. The panel used some commercial oil samples and actual oils produced in this study to determine the sensory terms. The panel determined 8 sensory descriptive terms. Descriptive terms, their definitions and references used are presented in Table 1. A 10 cm line scale from 1 at a minimum intensity to 10 at a maximum intensity was used for quantification. Samples were coded with 3 digit numbers and served in glasses to the panelists together with water, unsalted crackers, and expectoration cups. The analyses were carried out under daylight at room temperature in different days and sessions. Sensory analyses of the oils were replicated in randomized order.

A consumer test with 85 volunteer consumers was also completed. The appearance, aroma, flavor and general acceptance attributes of the oils were evaluated by using hedonic scale (1=dislike extremely, 5=like extremely). The samples were coded with 3 digit numbers and served in glasses to the consumers together with water, unsalted crackers and expectoration cups in different sessions, and the test was duplicated randomly.

2.9. Statistical Analyses

Cold pressing of the sour cherry and cherry kernels was replicated twice. For each replicate samples, the listed analyses were done at least in duplicate. Comparison of the two kernel oils for the analyses was accomplished by ANOVA and Tukey test. Sensory evaluation data were compared by using non-parametric Kruskal-Wallis and Dunn's test. Minitab Ver. 16.1.1 package software was used for statistical analyses [26]. The level of confidence was at least 95% in this study.

3. Results and Discussion

3.1. Properties of the Seeds and the Kernels

Some common physical properties of the sour cherry and cherry seeds and their kernels are presented in Table 2. There was no significant difference between the seeds for their color values. The seeds and their kernels could be observed in Figure 1. Clearly, these materials are not fully luminous, and have some yellowness and redness. The kernels had some color differences, and cherry kernels had higher redness and yellowness values (Table 2). The seed and kernel dimensions were also measured. Although the seeds were not significantly different, the cherry kernels were smaller than sour cherry kernels. They must depend on biotic factors. 1000-seed weight of the seeds and kernels were not statistically different. The meal: shell ratio was 0.15 for both sample. These data are provided for literature as a reference for future studies.

The proximate compositions of the two kernels are summarized in Table 3. These data would be important in determining the value of the waste seeds for various processing purposes. Clearly both sour cherry and cherry kernels are good sources of oil (20.17 and 18.33%) and protein (29.36 and 22.26%). Hence, both could be valorized for their oil and protein to be extracted and used as food or feed resources. There were differences only for the crude protein and ash contents, and sour cherry kernels contained higher amounts. In this study, the goal was to get their oils, but after cold pressing the oil, the meals could be used for protein extraction, and probably for dietary fiber production.

Yilmaz and Gökmen determined around 29.3% protein and 17% oil in some sour cherry kernels [17]. Similarly, Kamel and Kakuda measured around 31.7% crude protein and 41.9% crude oil in cherry kernels [14]. The differences among different studies might be due to genetic or agronomic factors.

3.2. Physico-Chemical Properties of the Oils

The most important physico-chemical properties of the cold press produced sour cherry (SCSO) and cherry seed oils (CSO) are given in Table 4. Oil yield of SCSO (55.95%) was greater than that of the CSO (51.30%). Although statistically not significant, the total crude oil content of the sour cherry seeds (20.27%) was a little higher than cherry seeds (18.33%), and this might be the reason of higher oil yield by cold pressing. Obviously, by cold pressing only 50-55% of the total oil was obtained. This could be very low in comparison with solvent extraction systems, which yields oils by around 90-95% [27]. In our previous studies, the same situation was observed that cold pressing oil yield is always lower, but it provides very high quality oils with all minor components and aromas retained [6, 8]. Hence, depending on the purpose of oil production, the extraction process can be selected. In this study, the goal was to establish cold pressing of the kernel oils and to characterize them for further possible applications.

The specific extinction values (E232 and E270) usually provides information about the storage conditions or oxidation status of the oils. In this study, these parameters provide insight about secondary oxidation products (dienes and trienes) accumulation of the oils. In fact, the cold pressed oils were immediately analyzed, but during pressing some time elapsed, which air was in contact with the oils. Further, during the seed storage, some inherent oxidation could have already occurred. These parameters were important in virgin oils, and usually used in commercial value determination of virgin olive oils [28]. The codex permits max 2.50 and 0.22 values of E232 and E270 extinctions for extra virgin olive oil [29]. Values for the SCSO and CSO are higher than the codex value, indicating some oxidation, or prolonged seed storage periods.

The specific gravity values were the same and 0.92. Oil refractive index and viscosity values were not different.

Refractive indices are similar to most oils, and indicate that the oils are wholesome. Viscosity values of the oils heavily depend on its fatty acids and minor components compositions, and may determine usage areas, and could be used for pump force calculations [27]. Refractive indices of SCSO as 1.469 [30], and CSO as 1.478 [16] were published.

The color values were not statistically different, and both oils are characterized by the low level of brightness, some green tones (negative a* values) and yellowness (positive b* values). The oil samples can be visually observed in Figure 1.

As the most important chemical parameters, the free fatty acidity (FFA) and acid numbers were presented in Table 4. CSO had higher values for both parameters than that of the SCSO. Since both oils were produced under the same processing conditions, these difference could be due to the nature of original seeds or seed storage conditions. Since FFA and acid value indicate the level of nonesterified fatty acids generated by hydrolysis, they also determine the consumer acceptability (high acid oils are quite sour) and refining losses, if they are refined [27]. The vegetable oils codex of Turkey indicates max acceptable acid value of 4.0 mg KOH/g oil for cold pressed oils [31]. Hence, these two oils could not be consumed as virgin oils and must go refining.

The peroxide and *p*-anisidine values are measured to determine the primary and secondary oxidation products, respectively. SCSO had significantly higher values for both oxidation parameters. The codex specifies max 15 meqO_2/kg oil for cold pressed oils [31], and SCSO exceeds this limit value. Overall, both cold pressed oils are not within the acceptable range for the most important chemical quality criteria. Since the seeds were got from the previous year harvest, and cold pressed oils were immediately analyzed, these values must be due to the genetic nature of the source material. Hence, cold pressed SCSO and CSO seems unsuitable as edible oils.

Oil characterization parameters, iodine number, saponification number and unsaponifiable matter contents were measured (Table 4) to give information about the saturation level, molecular weight and total minor components contents of the samples, respectively [27].

Iodine number of SCSO was lower (77.29) than CSO (99.69). Saponification numbers were not significantly different, and were 189.54 and 195.66 mg KOH/g oil, respectively.

Popa et al. provided the iodine value and saponification numbers for SCSO as 122.5 g I_2/100 g oil and 183 mg KOH/g [32].

The same two values for CSO were given as 116 g I_2/100 g oil and 198 mg KOH/g [30]. Although saponification numbers measured in this study concur with literature, the iodine numbers are much lower. This difference could be due to genetic differences or agronomic variations. The unsaponifiable matter contents of the samples were the same and 1.94% (Table 4). Unsaponifiable matter contents of 0.72% for SCSO [15], and 3.12% for CSO [30] were published. Clearly, source material differences for this matter is the determinant factor.

Table 1. The panel defined sensory descriptive terms and their standards

Descriptor	Definition	Reference
Fullness	Fatty films that covers the mouth space	Min: absent, Max: sunflower oil
Hay	Aromatics associated with hay or straw	Min: absent, Max: dry hay
Bitter	Taste stimulated by caffeine	Min: absent, Max: 0.5% caffeine solution in water
Astringent	Constriction and shrinking felt in mouth tissue	Min: absent, Max: 1.0% alum solution
Cherry syrup	The aroma perceived from cherry flavored cough syrup	Min: absent, Max: cherry flavored cough syrup
Fresh almond	Aromatics associated with almonds	Min: absent, Max: benzaldehyde
Menthol	Cooling effect felt in mouthspace	Min: absent, Max: menthol candy
Sweet aromatic	Aromatics associated with honey, molasses, sugar and maple syrups	Min: absent, Max: newly opened honey jar

Table 2. Properties of the sour cherry and cherry seeds and their kernels

	Sour cherry seed	Cherry seed	Sour cherry kernel	Cherry kernel
L value	42.30 ± 2.54^a	41.47 ± 2.50^a	46.57 ± 0.52^b	58.12 ± 0.63^a
a* value	7.55 ± 0.26^a	8.16 ± 0.51^a	6.84 ± 0.29^b	8.11 ± 0.20^a
b* value	18.61 ± 0.59^a	20.73 ± 1.14^a	23.85 ± 0.18^b	26.77 ± 0.30^a
Length (mm)	10.58 ± 0.25^a	10.89 ± 0.24^a	7.60 ± 0.23^a	7.61 ± 0.23^b
Thickness (mm)	6.99 ± 0.13^a	7.26 ± 0.18^a	3.90 ± 0.15^a	3.13 ± 0.18^b
Width (mm)	8.53 ± 0.19^b	9.39 ± 0.21^a	4.81 ± 0.06^a	4.35 ± 0.11^b
1000-seed weight (gr)	237.63 ± 4.70^a	247.33 ± 5.56^a	48.62 ± 2.71^a	55.36 ± 4.68^a
Meal/shell ratio	0.15 ± 0.02^a	0.15 ± 0.02^a	-	-

*Different superscript letters in the same line indicate significant differences between the seeds and their kernels ($p \leq 0.05$). Results are expressed as mean ± SE

Table 3. Proximate composition of the sour cherry and cherry kernels

	Sour cherry kernel	Cherry kernel
Moisture (%)	13.60 ± 0.07^a	12.67 ± 0.02^a
Water activity (25 °C)	0.34 ± 0.00^a	0.34 ± 0.00^a
Crude oil (% dw)	20.27 ± 1.25^a	18.33 ± 1.35^a
Crude protein (% dw)	29.36 ± 0.29^a	22.26 ± 0.51^b
Ash (%)	1.93 ± 0.03^a	1.80 ± 0.03^b

*Different superscript letters in the same line indicate significant differences between the kernels ($p \leq 0.05$)

Table 4. The physico-chemical properties of the sour cherry and cherry seed oils

Physical properties			Chemical properties	
	Sour cherry seed oil	**Cherry seed oil**	**Sour cherry seed oil**	**Cherry seed oil**
Oil yield (%)	55.95 ± 2.70[a]	51.30 ± 2.80[b]	Free fatty acidity (linoleic acid %)	2.86 ± 0.24[b]	9.99 ± 0.11[a]
Specific gravity (25 °C)	0.92 ± 0.00[a]	0.92 ± 0.00[a]	Acid number (mg KOH/g oil)	5.69 ± 0.47[b]	19.87 ± 0.21[a]
Specific extinctions (E232)	3.64 ± 0.12[a]	3.47 ± 0.08[a]	Peroxide value (meqO_2/kg oil)	16.32 ± 1.46[a]	9.29 ± 0.47[b]
Specific extinctions (E270)	2.04 ± 0.12[a]	1.69 ± 0.14[a]	*p*-Anisidine value	16.83 ± 0.68[a]	11.63 ± 1.01[b]
Refractive index (25 °C)	1.48 ± 0.00[a]	1.48 ± 0.00[a]	Iodine number (g I_2/100 g oil)	77.29 ± 1.58[b]	99.69 ± 0.83[a]
Viscosity (25 °C, cP)	71.45 ± 0.56[a]	71.22 ± 0.31[a]	Saponification number (mg KOH/g oil)	189.54 ± 1.46[a]	195.66 ± 1.20[a]
Color			Unsaponifiable matter (%)	1.94 ±0.02[a]	1.92 ± 0.02[a]
L value	26.63 ± 0.08[a]	25.96 ± 0.35[a]			
a* value	-2.22 ± 0.04[b]	-0.81 ± 0.34[a]	Total phenolics (mg gallic acid/100g oil)	0.42 ± 0.01[b]	0.71 ± 0.02[a]
b* value	11.14 ± 0.14[a]	11.61 ± 0.31[a]	Antioxidant capacity (mmol trolox/100 g oil)	9.00 ± 0.90[a]	10.40 ± 2.60[a]

*Different superscript letters in the same line indicate significant differences between the oils for each property ($p \leq 0.05$)

Table 5. The thermal properties of the sour cherry and cherry seed oils

		Sour cherry seed oil	**Cherry seed oil**
Melting	$Onset_m$ (°C)	-24.10 ± 0.34[a]	-24.70 ± 0.61[a]
	T_m (°C)	-21.00 ± 0.12[a]	-21.87 ± 0.09[a]
	ΔH_m (J/g)	2.95 ± 0.08[a]	2.63 ± 0.26[a]
Crystallization	$Onset_c$ (°C)	-13.21 ± 0.94[a]	-12.17 ± 0.03[a]
	T_c (°C)	-16.84 ± 0.49[a]	-14.92 ± 0.05[a]
	ΔH_c (J/g)	-0.32 ± 0.06[a]	-0.43 ± 0.06[a]
	OIT (130 °C, min)	3.15 ± 0.01[b]	4.23 ± 0.12[a]

*Different superscript letters in the same line indicate significant differences between the oils ($p \leq 0.05$)

Although the total phenolic content of CSO was higher than that of the SCSO, their antioxidant capacity values were not significantly different (Table 4). Yilmaz and Gökmen measured the total phenolics and antioxidant capacity of supercritical fluid and solvent extracted SCSO as 6.60-9.61 and 19.34-27.87 mgGAE/L, and 1.44-2.20 and 2.06-2.23 mmolTEAC/L, respectively [17]. Since they measured these values per liter of the oil sample, it is not possible for direct comparison. Both values were measured in 100 g oil samples in this study, and after unit conversion, it seems that the values are similar. In another study, total phenolics content of 6.28 meqGA/kg and antioxidant capacity of 96.23% DPPH were given for CSO [16].

3.3. Thermal Properties of the Oils

The onset and peak temperatures and enthalpy values of both oils for melting and crystallization were measured (Table 5). There was no significant difference between the samples for the thermal parameters.

Fully crystallized oil (at – 50 °C), starts melting at around – 24 °C and completely melts at around – 21 °C. Totally liquid oils start crystallization at around – 12 °C, and crystal formation completes at around – 14 and -16 °C, respectively. This shift between melting and crystallization temperatures is a common phenomenon in unsaturated oils [33]. Since literature lack for thermal parameters of these oils, data provided in this study would be important. The oxidation induction times (OIT values as min) determined at 130 °C provides information about thermal oxidation stability of the oils. CSO is more stable (4.23 min) than SCSO (3.15 min). Korlesky et al. indicated 30.3 min OIT at 130 °C for SCSO [15]. This is quite higher than the value (3.15 min) measured in this study.

3.4. Fatty Acid, Sterol and Tocopherol Compositions of the Oils

The fatty acids, sterols and tocopherols compositions of the SCSO and CSO are listed in Table 6.

There was no significant difference in the fatty acid compositions of the oils. Six fatty acids were quantified, with the majority being linoleic (40-19-42.16%), oleic (35.28-39.46%) and palmitic (12.45-19.51%), respectively. These two oils are highly unsaturated, and unsaturated fatty acids comprise around 78-86% of total fatty acids. Yilmaz and Gökmen identified fatty acid composition of SCSO as 6.4% palmitic, 1.2% stearic, 46.3% oleic, 41.5% linoleic and 4.6% linolenic acid [17]. Except for palmitic acid, our result concurs with theirs. In another study, the fatty acids of SCSO were identified as 35.50-46.06% linoleic, 25.25-45.30% oleic, 7.43-15.76% α-eleostearic and 5.06-7.38% palmitic acid [13]. Again, except α-eleostearic acid, results concur. Similarly, fatty acid composition of CSO was given by Bernardo-Gil et al. as 40.84% linoleic, 32.64% oleic, 10.11% eleostearic, 5.26% palmitic and 2.15% stearic acid [10]. Generally, the results of this study concur with literature.

Four sterols were quantified in the oil samples (Table 6). For all sterols quantified, SCSO had significantly higher concentrations than those of the CSO. The main sterol was β-sitosterol (410.00 and 317.75 mg/100 g) in both samples, respectively. In different sour cherry seed oils, the total sterol content was found as 313.6-1041.3 mg/100 g with β-sitosterol as the major (77-82%) sterol [13]. Bernardo-Gil et al. identified 83.41% β-sitosterol, 7.55% Δ5-avenasterol and 3.85% stigmasterol in CSO [10]. Results of this study are in a good agreement with literature.

Three tocopherols ((δ-, γ-, and α-tocopherol) with majority of γ-tocopherol (around 701.0 mg/kg) were quantified in both oils. There was no significant difference between the samples. Literature indicated 376-428 mg/L total tocopherol for solvent extracted, and 312-381 mg/L total tocopherol for supercritical fluid extracted SCSO samples [17]. Also, Gornas et al. reported 3.03-4.96% α-, 0.01-0.11% β-, 32.26-37.51% γ- and 0.95-1.69% δ-tocopherol for CSO [12]. Generally, the findings concur.

3.5. Volatile Compositions of the Oils

Sixteen different volatile compounds in SCSO and 12 different volatiles in CSO were identified and quantified (Table 7). For both samples, benzaldehyde, ethylamine, benzyl alcohol, and pentanal were found in higher concentrations.

The most profound aroma descriptors with the quantified volatiles were almond, ammonia, floral, wine, fruity, and vinegar. It is well known in aroma science that concentration of a volatile is not very important by itself. In fact, the odor threshold value is the determining factor of how a sample is sensed for its aroma or odor attribute. By definition, odor threshold is the lowest concentration of a volatile compound where, its smell could be sensed by humans. It is independent of the concentration, and compounds could be sensed very definitely at very low concentrations or vice versa [25]. Although the odor threshold values of the most common aromatic volatiles in water and/or alcohol media was published, the literature lacks the data for many other volatile compounds especially in oil media. Hence, in this study and in similar many studies in the literature, volatile composition data have been published. This data is quite important to indicate which volatiles at what concentrations are present in a certain sample. Further, the association of volatiles data with descriptive sensory analysis and consumer tests is essential to evaluate an oil sample for edible purposes [6].

There is no data found in literature about the volatiles compositions of the SCSO and CSO. Only one study reported the volatiles of black cherry (*Prunus serotina*) seeds [34]. Raw and roasted seeds were determined to have 59 and 99 different volatiles, which mostly comprise aldehydes, alcohols, ketones, carboxylic acids, esters, hydrocarbons, and pyrazines. Benzaldehyde, pentanal, acetic acid, benzyl alcohol were the common compounds between the studies. Clearly, benzaldehyde with its almond and nutty aroma description is the key compounds in cherry genus seeds and the oils extracted from their kernels. Overall, this study provides very important volatiles data for the literature.

3.6. Sensory Analysis of the Oils

The panel evaluated sensory descriptive properties of the SCSO and CSO with 8 different definition terms on a 10-cm line scale with QDA technique, and the results are presented in spider web graphical format in Figure 2.

The ‘fullness’ term indicates the fatty film covered in mouth space by the oils, and both oils scored around 6.0-6.42 values. It seems that they are lower compared with the reference (sunflower oil) which indicates a 10.0 score.

Table 6. The fatty acid, sterol and tocopherol compositions of the sour cherry and cherry seed oils

	Sour cherry seed oil	**Cherry seed oil**
Fatty acid (%)		
Palmitic (C16:0)	19.51 ± 4.17[a]	12.45 ± 1.40[a]
Palmitoleic (C16:1)	1.32 ± 0.36[a]	0.81 ± 0.08[a]
Stearic (C18:0)	1.31 ± 0.11[a]	1.54 ± 0.05[a]
Oleic (C18:1 n-9)	35.28 ± 2.16[a]	39.46 ± 0.40[a]
Linoleic (C18:2 n-6)	40.19 ± 1.97[a]	42.16 ± 0.32[a]
Eicosapentaenoic (C20:5)	2.41 ± 0.28[a]	3.49 ± 0.72[a]
ΣSFA	20.82 ± 4.28[a]	13.99 ± 1.45[a]
ΣMUFA	36.60 ± 2.52[a]	40.27 ± 1.20[a]
ΣPUFA	42.60 ± 2.25[a]	45.75 ± 1.04[a]
Sterol (mg/100 g oil)		
Campesterol	18.55 ± 0.55[a]	9.9 ± 0.10[b]
β-Sitosterol	410.00 ± 2.01[a]	317.75 ± 0.75[b]
Sitostanol	15.20 ± 0.10[a]	11.05 ± 0.25[b]
Δ5-Avenasterol	21.60 ± 0.50[a]	16.55 ± 0.55[b]
Total sterol	465.35 ± 2.05[a]	355.25 ± 1.45[b]
Tocopherol (mg/kg oil)		
δ-Tocopherol	76.15 ± 0.26[b]	85.84 ± 1.46[a]
γ-Tocopherol	701.42 ± 2.73[a]	701.58 ± 2.18[a]
α-Tocopherol	39.07 ± 0.23[a]	37 ± 0.10[b]
Total tocopherol	816.64 ± 2.70[a]	824.42 ± 3.74[a]

*Different superscript letters in the same line indicate significant differences between the oils ($p \leq 0.05$)

Table 7. The volatile composition of sour cherry and cherry seed oils

No	**RI**	**Volatile**	**Aroma description**	**Sour cherry seed oil (µg/kg oil)**	**Cherry seed oil (µg/kg oil)**
1	600	Acetic acid	Vinegar, sour	507.92 ± 7.62b	788.70 ± 5.67a
2	675	3-hydroxy butanoic acid	-	160.97 ± 11.55	-
3	699	Pentanal	Fermented, wine	789.72 ± 10.50b	867.54 ± 2.73a
4	785	Ethanol, (2-vinyloxy)	-	174.15 ± 10.76	-
5	825	6-heptane	-	169.55 ± 3.05	
6	885	Ethylamine	Ammonia	1677.32 ± 18.80a	714.17 ± 8.30b
7	960	Benzaldehyde	Almond, nutty	16842.97 ± 103.02b	21538.53 ± 6.47a
8	1006	Hexanoic acid	Cheesy, sour	255.69 ± 7.58	-
9	1027	D-Limonene	Citrus	93.2 ± 9.90	-
10	1038	Benzyl alcohol	Floral	1081.96 ± 13.05a	668 ± 8.02b
11	1086	Pyrazine, tetramethyl	Nutty, cacao	84.38 ± 1.99b	299.22 ± 2.17a
12	1111	Phenylethyl Alcohol	Sweet, floral	139.86 ± 12.35	-
13	1135	Acetic acid, phenylmethyl ester	-	321.82 ± 3.80a	225.28 ± 0.43b
14	1216	2,4-nonadienal (E,E)-	Fatty, bees was, cucumber, melon	249.33 ± 7.29a	214.95 ± 1.17b
15	1293	2,4-decadienal	Citrus, grassy	67.15 ± 4.72	-
16	1326	Linoleic acid, ethyl ester	Oily, fruity	51.04 ± 5.89	-
17	1378	1-Butanol, 3-methyl, acetate	-	-	219.03 ± 1.44
18	991	Furan, 2-pentyl	Fruit, waxy, caramel	-	374.9 ± 2.31
19	1030	Limonene	Citrus, herbal	-	236.60 ± 1.07
20	1335	Benzoic acid, ethyl ester	Mint, fruity, sweet	-	142.45 ± 1.62

*Different superscript letters in the same line indicate significant differences between the oils ($p \leq 0.05$)

This might be due to the aroma of the oils, which are not quite similar to sunflower or other edible liquid oil, but rather resembles a cough syrup aroma. The 'hay' score of CSO was higher (2.32) than that of the SCSO (1.77). It is associated with dry straw, and usually perceived as a negative sensory term [35].

There was no significant difference between the samples for 'bitter' scores, and both were low (1.31-1.92). In our previous study with grapefruit seed oil, the bitter scores were fairly high, and hence, bitterness seems not a problem in these oils [8].

Similar findings also exist for the 'astringent' term. 'Cherry syrup' was defined as the aromas perceived from cherry flavored cough syrup (Table 1), and it was quite typical for these two oil samples. SCSO had a significantly higher score (2.55) than that of the CSO (1.86). Since the cough syrups are usually flavored with cherry extracts, the panel defined this particular attribute with the term chosen. Further, this sensory attribute could be related with the benzaldehyde, acetic acid, ethylamine and benzyl alcohol volatiles listed in Table 7. Generally, panelist indicated a negative perception with cherry syrup attribute, and indicated that it should not be present in an edible oil. The 'fresh almond' was the dominant attribute with 4.0 and 5.7 scores in SCSO and CSO, respectively (Figure 2). This attribute is completely related with the benzaldehyde volatile quantified in the samples. In fact, the concentration of benzaldehyde was higher in CSO than SCSO (Table 7), and it was linearly related to the sensory scores. Most of the panel members identified this attribute as positive in terms of their preference. 'Menthol' was the cooling effect felt in mouthspace, and took scores of 1.54 and 1.33 for the samples, respectively.

Generally, common edible liquid oils lack such an attribute, but some cold pressed oils like grapefruit seed oil [8] had it.

Since it is not a usual sensation in edible oils, the panel indicated it as a negative attribute. Interestingly, these oil samples showed important scores (2.54 and 2.50) of 'sweet aromatic' descriptor. It was related with aromatics associated with honey, molasses, sugar and maple syrups, once their jars opened, this aroma is perceived. Overall, SCSO and CSO are quite interesting samples described with uncommon sensory terms like cherry syrup, menthol and sweet aromatic. Since the literature lack this information, the data provided in Figure 2 would be very valuable for those who interested to use these oils in various products.

Finally, consumer perceptions of the two oils were tested with 85 volunteer consumers with a 5-point hedonic scale (1=dislike extremely, 5=like extremely) for appearance, aroma, flavor and general acceptance (Figure 3). For all attributes, SCSO had a little higher scores than CSO. Generally, both oil samples had scores around 3.0-3.5 for the attributes tested. This result indicates that consumers perceive these samples at the neutrality point, which indicates a neither like nor dislike. For an edible cold press oil, this point could be accepted as not good enough. Hence, edible consumption of these oils seems unsuitable based on consumer test results. Other non-edible application could be suggested.

Figure 1. The sour cherry and cherry seeds, their kernels, and their cold press produced oils (a: sour cherry; b: cherry)

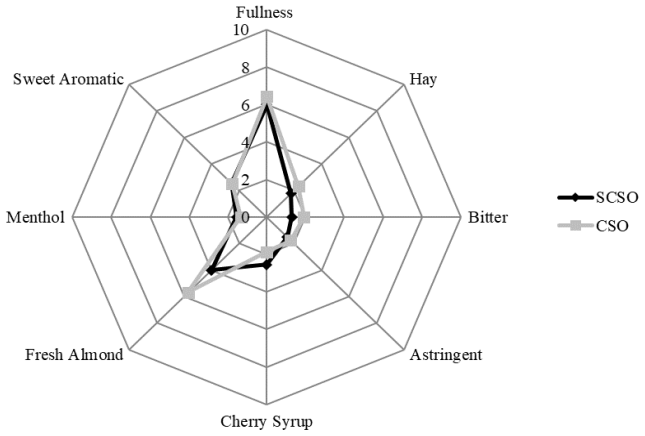

Figure 2. The descriptive sensory properties of the SCSO and CSO samples

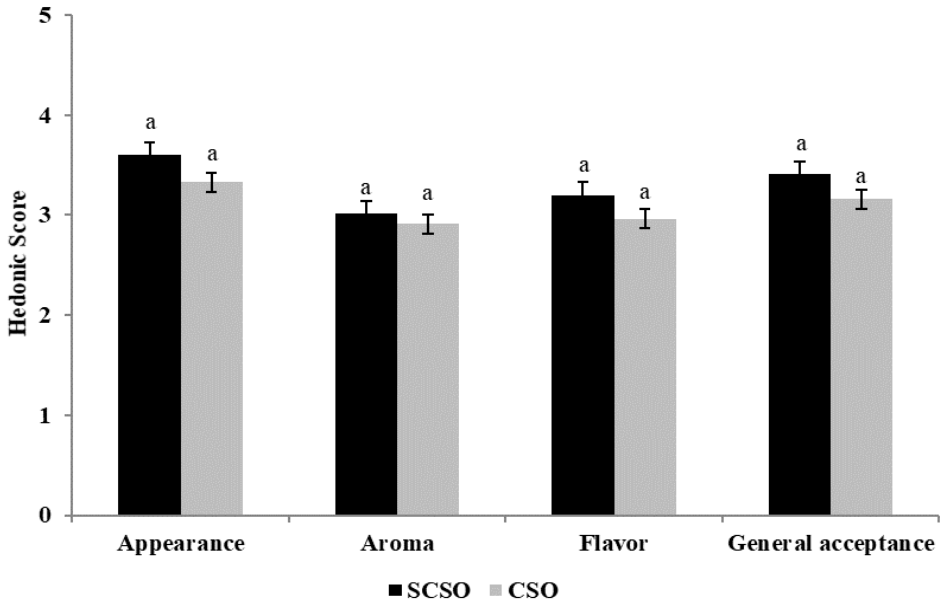

Figure 3. The consumer hedonic scores for the SCSO and CSO samples

4. Conclusions

This study proved that sour cherry and cherry seeds could be valorized by generating the kernel oils through cold press technique. Further, the meal after cold pressing could be utilized for protein and/or fiber extraction. The cold press produced SCSO and CSO were evaluated in detail with common oil analysis parameters, their main compositions, volatile analysis and sensory analysis. Most data are provided for the first time in the literature. Since consumer test results indicated the unsuitability of these oils for direct edible consumption, utilization in nutraceutical, cosmetic, or energy areas would be suggested in future studies.

Compliance with Ethics Requirements. Authors declare that they respect the journal's ethics requirements. Authors declare that they have no conflict of interest and all procedures involving human or animal subjects (if exist) respect the specific regulation and standards.

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