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Proceeding Paper

The Quality Assessment of Oils Obtained from Berry Fruit Seeds Using Pressurized Liquid Extraction †

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Abstract: Berry fruit seeds should be treated as a valuable waste product of the fruit industry. In the following study, oils from cranberry, black currant, red currant, strawberry and chokeberry seeds were extracted by conventional and pressurized liquid extraction. The quality of oils was assessed by determining oxidative stability (onset and maximum time of induction) with the use of pressure differential scanning calorimetry, fatty acids composition by gas chromatography and health indices, such as atherogenicity, thrombogenicity and hypocholesterolemic indexes. Additionally, health-promoting index was calculated. It was found that the fatty acid profile was not affected when pressurized liquid extraction was used. The major fatty acids in the studied oils were linoleic acid ranging from 36% for cranberry seed oil to 69% for chokeberry seed oil, followed by α-linolenoic acid in the case of cranberry, strawberry and red currant seed oils or by oleic acid for chokeberry and black currant seed oils. The oxidative stability of fats extracted with the use of pressurized solvent was significantly lower compared to oils obtained using the conventional extraction process, e.g., the maximum induction time for conventionally extracted chokeberry seed oil was 40.74 $\pm$ 0.66 min and 9.24 $\pm$ 0.57 min when pressurized liquid extraction was applied. The studied oils had low values of atherogenicity and thrombogenicity indexes, which, when combined with high values of hypocholesterolemic index, qualifies them as high nutritional quality oils. However, further studies regarding the process optimization are needed in order to obtain oils with improved quality, especially better oxidative stability.

Keywords: accelerated solvent extraction; pressurized liquid extraction; oil extraction; fruit seeds; oxidative stability; PDSC; GC

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1. Introduction

The conventional methods of extractions are being gradually replaced by novel, alternative extraction methods, which may be beneficial in terms of energy and solvent consumption and selectivity of the process. One of the techniques considered as 'green' is pressurized liquid extraction (PLE), which involves heating a liquid solvent to a temperature above its boiling point and, at the same time, applying high pressure to let the solvent remain liquid. The main advantage of the PLE technique is that increased temperature improves the diffusion process and solubility of the extracted molecules with a decrease in the amount of solvent used. High pressure also promotes mass transfer during the process.

Both high temperature and high pressure reduce the surface tension of the solvent, which also influences improved extraction efficiency [1].

The main objective of this work was to evaluate the possibility of applying PLE to obtain oil from berry seeds and to study the effect of PLE on the quality of oil, with special regard to the oxidative stability and fatty acids profile of the fat fraction. For comparison, conventional extraction of oils from berries' seeds was performed, followed by studies of their quality characteristics.

2. Materials and Methods

2.1. Materials

The seeds of cranberry, black currant, red currant, strawberry and chokeberry were used for analysis. Seeds were ground in a laboratory tube mill (IKA Werke, Staufen im Breisgau, Germany) at 25,000 rpm for 30 s.

2.2. Pressurized Liquid Extraction (PLE) of Oil

Ground samples of 5 g of seeds were mixed with diatomaceous earth and were placed in cells made from stainless steel. The process was conducted following the methodology described by Dobroslavić et al. [2] in a Dionex ASE 350 Accelerated Solvent Extractor (Thermo Fisher Scientific Inc., Sunnyvale, CA, USA) in 4 cycles with n-hexane as a solvent. The temperature of the oven was set at 150 °C and the static extraction time was 5 min. The pressure was 10.34 MPa, the nitrogen purge was 30 s and the volume flush was set at 50%. Glass vials with Teflon septa were used to collect the extracts. The solvent was removed using a vacuum evaporator, and oils were dried in a nitrogen atmosphere to remove residual hexane. Oil yield values were calculated according to Equation (1):

$$Y = \frac{m_o\ [g]}{m_s\ [g]} \times 100\%, \quad (1)$$

where Y—oil yield; m_o—mass of oil; m_s—initial mass of powdered seeds.

2.3. Conventional Extraction (CE) of Oil

The extraction of oil in Soxhlet apparatus was conducted based on the methodology described by Dobson et al. [3] with modifications. Ground samples of 5 g of seeds were put into the apparatus in a paper thimble with 150 mL of n-hexane. The extraction was carried out in 5 cycles; then, solvent was evaporated. Obtained oils were dried in a nitrogen atmosphere and oil yield was calculated as for the PLE method.

2.4. Resistance to Oxidation

The oxidative stability of oils was determined using pressurized differential scanning calorimetry (PDSC), as described by Bryś et al. [4], at 120 °C. A DSC Q20 apparatus (TA Instruments, New Castle, DE, USA) was used. An aluminum pan filled with oil and an empty pan used as a reference were placed in the cell under oxygen atmosphere at an initial pressure set at 1400 kPa. The oxidation reaction induction maximum (OIT) and onset times (OOT) of examined oils were determined.

2.5. Fatty Acids Analysis

The fatty acids profile of extracted oils was determined after converting fatty acids to fatty acid methyl esters (FAME) according to the PN-EN ISO:2001 standard method [5], followed by gas chromatography using YL6100 GC apparatus (Young Lin Bldg., Anyang, Hogye-dong, Republic of Korea), according to the previously described method [6]. The results are expressed as a percentage of each fatty acid.

2.6. Health Indices of Oils

The health indices based on the fatty acids profile, including the PUFA/SFA ratio, indexes of atherogenicity (IA) and of thrombogenicity (IT), developed by Ulbritcht and

Southgate [7], hypocholesterolemic/hypercholesterolemic ratio (HH) developed by Santos Silva et al. [8] and health-promoting index (HPI) proposed by Chen et al. [9], were counted according to Equations (2)–(5):

$$\mathrm{IA} = \frac{C12:0 + (4 \times C14:0) + C16:0}{\sum UFA} \quad (2)$$

$$\mathrm{IT} = \frac{C14:0 + C16:0 + C18:0}{0.5 \times \sum MUFA + (0.5 \times \sum n-6\ PUFA) + (3 \times \sum n-3\ PUFA) + \frac{n-3}{n-6}} \quad (3)$$

$$\mathrm{HH} = \frac{cis - C18:1 + \sum PUFA}{C12:0 + C14:0 + C16:0} \quad (4)$$

$$\mathrm{HPI} = \frac{\sum UFA}{C12:0 + 4 \times C14:0 + C16:0} \quad (5)$$

2.7. Statistical Analysis

Collected results are presented as mean value ± standard deviation. The one-way ANOVA and post hoc Tukey's test with a p-value of 0.05 were chosen to consider significant differences, and analyses were performed using Statistica 13.3 Software (StatSoft, Kraków, Poland).

3. Results and Discussion

3.1. Extraction Efficiency

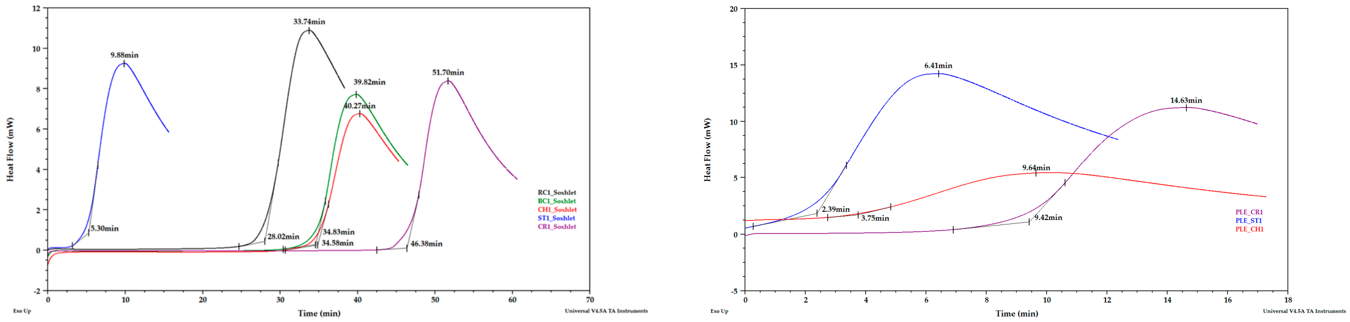
The yields of oil extractions are presented in Table 1. In the case of conventional extraction, all the yield values, except the red currant seed oil, were lower than oil yields of PLE. Usage of high temperatures during the PLE process was responsible for an increased efficiency in the extraction as it caused overcoming cohesive interactions between molecules and decreased the activation energy required for molecules' release. Therefore, the surface tension of n-hexane was consequently lowered by the enhanced temperature, so the oil dissolution in hexane was accelerated. Also, the high pressure forced n-hexane to penetrate the matrix extensively [1].

Table 1. Oil yield in pressurized liquid extraction and conventional extraction.

Oil Source	PLE Oil Yield [%]	CE Oil Yield [%]
Cranberry	16.00	11.52
Strawberry	13.53	10.94
Chokeberry	5.08	3.59
Black currant	7.60	3.31
Red currant	1.70	5.84

3.2. Oxidative Stability of Oils

Examples of curves obtained in one run of the PDSC study are presented in Figure 1. The results of the PDSC study are presented in Table 2. Generally, oils obtained by applying pressurized liquid extraction were characterized by low OIT and OOT. The OIT of pressurized-liquid extracted black currant and red currant seed oils was undetectable as the peak was evident right at the beginning of the PDSC diagram. Based on the obtained results, it can be stated that conventionally extracted cranberry seed oil with an OOT equal to 44.67 ± 2.49 min and OIT equal to 50.20 ± 2.12 min was the most stable. Also, in the case of PLE oils, cranberry seed oil was significantly more resistant to oxidation than others.



(**A**) (**B**)

Figure 1. Examples of PDSC diagrams of conventionally extracted oils (**A**) and PLE oils (**B**); RC—red currant, BC—black currant, CH—chokeberry, ST—strawberry, CR—cranberry.

Table 2. Onset (OOT) and maximum (OIT) induction time of oils extracted using pressurized-liquid extraction and conventional extraction.

Oil Source	PLE Oils		CE Oils	
	OOT [min]	OIT [min]	OOT [min]	OIT [min]
Cranberry	8.44 ± 1.39 ^{B}	13.94 ± 0.98 ^{C}	44.67 ± 2.49 ^{a}	50.20 ± 2.12 ^{a}
Strawberry	3.06 ± 0.95 ^{A}	6.71 ± 0.42 ^{A}	6.34 ± 1.78 ^{c}	10.80 ± 1.30 ^{c}
Chokeberry	3.04 ± 1.03 ^{A}	9.24 ± 0.57 ^{B}	35.21 ± 0.52 ^{b}	40.74 ± 0.66 ^{b}
Black currant	-	-	32.84 ± 2.73 ^{b}	37.91 ± 2.70 ^{b}
Red currant	-	-	27.64 ± 0.54 ^{b}	33.31 ± 0.62 ^{b}

Mean values with different letters (A–C and a–c) in the columns are significantly different at α = 0.05.

Comparing the oxidative stability of conventionally extracted oils to other plant-derived oils, it can be seen that the studied oils were characterized by lower OIT, measured in PDSC analysis at 120 °C, than rapeseed oil with an OIT at approximately 66–74 min [10,11]. The results obtained for PLE oils in the following study comply with the results obtained by De Mello et al. [12], who studied PL-extracted crambe seed oil. Applying higher temperatures during the process resulted in higher oil yield, sterols and γ-tocopherol content; however, the oxidative stability of the oil was lower, compared to commercial oil.

The oils' low resistance to oxidation when applying the PLE method may occur due to the high selectivity of the accelerated solvent extraction. Thus, possibly the only molecules extracted in the PLE were fats, without accompanying antioxidant compounds. In addition, oils by themselves might have been oxidized due to severe conditions of extraction [1,4]. Another reason for lowering the OIT could be the ability of high-temperature solvent to decrease the activation energy; therefore, the oxidation reaction may be initiated more easily [1].

3.3. Fatty Acids Profile and Health Indices

The summarized results of the fatty acids profile and counted health indices based on the Chen and Liu review [13] are presented in Table 3. Independently of the applied extraction method, the dominant fatty acid in the examined oils was linoleic acid (C18:2 n-6). The contribution of the sum of SFA, MUFA and PUFA in the fatty acids profile was similar. The differences between oil sourced from the same berry fruit seeds were only slight; however, even slight changes in the fatty acid profile affect the health indices of fat. Fatty acids profiles obtained in the following study were in agreement with those previously published [14,15].

Table 3. Fatty acid profile [%] of extracted oils and nutritional indices of oils based on their fatty acid profile.

	Fatty Acids	Cranberry Seed Oil		Strawberry Seed Oil		Chokeberry Seed Oil		Black Currant Seed Oil		Red Currant Seed Oil	
		PLE	CE	PLE	CE	PLE	CE	PLE	CE	PLE	CE
SFA	16:0	5.84 ± 0.06	5.74 ± 0.05	5.54 ± 0.01	5.07 ± 0.04	6.38 ± 0.04	5.22 ± 0.31	9.14 ± 0.11	6.98 ± 0.01	7.50 ± 0.04	5.88 ± 0.06
	18:0	1.23 ± 0.08	1.31 ± 0.08	2.00 ± 0.12	1.98 ± 0.13	1.63 ± 0.03	1.48 ± 0.01	2.62 ± 0.04	1.97 ± 0.03	1.65 ± 0.00	1.56 ± 0.01
	∑SFA	7.06 ± 0.14 [a]	7.04 ± 0.03 [a]	7.53 ± 0.11 [b]	7.05 ± 0.09	8.01 ± 0.01 [b]	6.70 ± 0.30 [a]	11.75 ± 0.07 [b]	8.95 ± 0.04 [a]	9.15 ± 0.04 [b]	7.43 ± 0.06 [a]
MUFA	16:1	0.11 ± 0.01	0.11 ± 0.01	0.23 ± 0.03	0.22 ± 0.02	0.18 ± 0.00	0.18 ± 0.01	0.21 ± 0.01	0.14 ± 0.01	0.36 ± 0.01	0.16 ± 0.00
	18:1 n-9	23.52 ± 0.03	24.01 ± 0.08	18.79 ± 0.08	18.31 ± 0.10	17.38 ± 0.06	17.99 ± 0.05	20.51 ± 0.04	15.86 ± 0.02	13.73 ± 0.01	11.98 ± 0.00
	∑MUFA	23.63 ± 0.01 [a]	24.11 ± 0.08 [b]	19.02 ± 0.11 [b]	18.53 ± 0.12 [a]	17.56 ± 0.06 [a]	18.16 ± 0.04 [a]	20.71 ± 0.03 [b]	16.00 ± 0.01 [a]	14.09 ± 0.03 [b]	12.14 ± 0.00 [a]
PUFA	18:2 n-6	36.35 ± 0.04	36.40 ± 0.06	44.88 ± 0.09	44.84 ± 0.11	67.23 ± 0.07	69.38 ± 0.06	45.03 ± 0.11	45.82 ± 0.12	38.54 ± 0.01	40.30 ± 0.02
	18:3 n-6	0.12 ± 0.02	0.12 ± 0.01	0.12 ± 0.01	0.10 ± 0.00	n.d.	n.d.	8.72 ± 0.02	12.08 ± 0.06	4.00 ± 0.01	4.27 ± 0.01
	18:3 n-3	31.80 ± 0.11	31.07 ± 0.04	28.46 ± 0.14	29.49 ± 0.08	1.99 ± 0.06	0.87 ± 0.01	10.15 ± 0.06	13.19 ± 0.01	31.48 ± 0.09	32.77 ± 0.04
	∑PUFA	68.27 ± 0.05 [b]	67.59 ± 0.11 [a]	73.46 ± 0.22 [a]	74.43 ± 0.20 [b]	69.22 ± 0.01 [a]	70.24 ± 0.07 [b]	63.89 ± 0.03	71.08 ± 0.06 [b]	74.01 ± 0.07 [a]	77.33 ± 0.07 [b]
	Other	1.04 ± 0.06	1.28 ± 0.01	n.d.	n.d.	5.23 ± 0.06	4.90 ± 0.18	3.67 ± 0.08	3.98 ± 0.03	2.76 ± 0.06	3.10 ± 0.01
	Health indices of oils based on fatty acid profile										
	PUFA/SFA	9.67	9.60	9.75	10.56	8.65	10.44	5.44	7.95	8.09	10.41
	IA	0.06	0.06	0.06	0.05	0.07	0.06	0.11	0.08	0.09	0.07
	IT	0.06	0.06	0.06	0.06	0.16	0.11	0.17	0.11	0.07	0.06
	HH	35.22	35.79	16.66	18.10	13.58	16.90	9.24	12.46	11.71	15.19
	HPI	15.75	15.99	16.71	18.35	13.61	16.93	9.26	12.48	11.75	15.23

PUFA/SFA—polyunsaturated fatty acid/saturated fatty acid ratio; IA—index of atherogenicity; IT—index of thrombogenicity; HH—hypocholesterolemic/hypercholesterolemic ratio; HPI—health-promoting index; n.d.—not detected; mean values with different letters (a–b) in the rows are significantly different at $\alpha = 0.05$, among oils from the same seeds.

4. Conclusions

Pressurized liquid extraction is a novel, green technique of separation which can be successfully used to extract oil from berry fruit seeds. Although the yield of the extraction conducted using the pressurized solvent was acceptable and the fatty acids profile was not affected, the oxidative stability of fats was significantly lower compared to oils obtained via conventional extraction. However, applying different conditions may be beneficial and may lead to obtaining oils with better qualitative properties. The studied oils were characterized by low values of atherogenicity and thrombogenicity indexes, which, when combined with high values of hypocholesterolemic index, allow berry fruit seeds oils to be considered as important elements of the dietoprophylaxis and dietotherapy of cardiovascular diseases. Further studies regarding the process optimization are needed in order to obtain oils with improved quality, especially better oxidative stability.

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References

1. Mustafa, A.; Turner, C. Pressurized liquid extraction as a green approach in food and herbal plants extraction: A review. *Anal. Chim. Acta* **2011**, *703*, 8–18. [CrossRef] [PubMed]
2. Dobroslavić, E.; Elez Garofulić, I.; Šeparović, J.; Zorić, Z.; Pedisić, S.; Dragović-Uzelac, V. Pressurized Liquid Extraction as a Novel Technique for the Isolation of *Laurus nobilis* L. Leaf Polyphenols. *Molecules* **2022**, *27*, 5099. [CrossRef]
3. Dobson, G.; Shrestha, M.; Hilz, H.; Karjalainen, R.; McDougall, G.; Stewart, D. Lipophilic components in black currant seed and pomace extracts. *Eur. J. Lipid Sci. Technol.* **2011**, *114*, 575–582. [CrossRef]
4. Bryś, J.; Wirkowska, M.; Górska, A.; Ostrowska-Ligęza, E.; Bryś, A. Application of the calorimetric and spectroscopic methods in analytical evaluation of the human milk fat substitutes. *J. Therm. Anal. Calorim.* **2014**, *118*, 841–848. [CrossRef]
5. *Polish Norm: PN-EN ISO: 5509:2001*; Oil and Vegetable and Animal Fats. Polish Committee for Standardization: Warsaw, Poland, 2001.
6. Piasecka, I.; Górska, A.; Ostrowska-Ligęza, E.; Kalisz, S. The Study of Thermal Properties of Blackberry, Chokeberry and Raspberry Seeds and Oils. *Appl. Sci.* **2021**, *11*, 7704. [CrossRef]
7. Ulbricht, T.L.V.; Southgate, D.A.T. Coronary heart disease: Seven dietary factors. *Lancet* **1991**, *338*, 985–992. [CrossRef] [PubMed]
8. Santos-Silva, J.; Bessa, R.J.B.; Santos-Silva, F. Effect of genotype, feeding system and slaughter weight on the quality of light lambs: II. Fatty acid composition of meat. *Livest. Prod. Sci.* **2022**, *77*, 187–194. [CrossRef]
9. Chen, S.; Bobe, G.; Zimmerman, S.; Hammond, E.G.; Luhman, C.M.; Boylston, T.D.; Freeman, A.E.; Beitz, D.C. Physical and sensory properties of dairy products from cows with various milk fatty acid compositions. *J. Agric. Food Chem.* **2004**, *52*, 3422–3428. [CrossRef] [PubMed]
10. Kowalska, D.; Kostecka, M.; Tarnowska, K.; Kowalski, B. Oxidative stabilities of enzymatically interesterified goose fat and rapeseed oil blend by rancimat and PDSC. *J. Therm. Anal. Calorim.* **2014**, *115*, 2063–2070. [CrossRef]
11. Symoniuk, E.; Ratusz, K.; Krygier, K. Comparison of the oxidative stability of cold-pressed rapeseed oil using Pressure Differential Scanning Calorimetry and Rancimat methods. *Eur. J. Lipid Sci. Technol.* **2017**, *119*, 1600182. [CrossRef]
12. de Mello, B.T.F.; Iwassa, I.J.; Cuco, R.P.; dos Santos Garcia, V.A.; da Silva, C. Methyl acetate as solvent in pressurized liquid extraction of crambe seed oil. *J. Supercrit Fluids* **2019**, *145*, 66–73. [CrossRef]
13. Chen, J.; Liu, H. Nutritional Indices for Assessing Fatty Acids: A Mini-Review. *Int. J. Mol. Sci.* **2020**, *21*, 5695. [CrossRef]

14. Bederska-Łojewska, D.; Pieszka, M.; Marzec, A.; Rudzińska, M.; Grygier, A.; Siger, A.; Cieślik-Boczula, K.; Orczewska-Dudek, S.; Migdał, W. Physicochemical Properties, Fatty Acid Composition, Volatile Compounds of Blueberries, Cranberries, Raspberries, and Cuckooflower Seeds Obtained Using Sonication Method. *Molecules* **2021**, *26*, 7446. [CrossRef]
15. Pieszka, M.; Migdał, W.; Gąsior, R.; Rudzińska, M.; Bederska-Łojewska, D.; Pieszka, M.; Szczurek, P. Native Oils from Apple, Blackcurrant, Raspberry, and Strawberry Seeds as a Source of Polyenoic Fatty Acids, Tocochromanols, and Phytosterols: A Health Implication. *J. Chem.* **2015**, *2015*, 659541. [CrossRef]