Croat. J. Food Sci. Technol. (2018) 10 (2) 197-205

Croatian Journal of Food Science and Technology

journal homepage: www.ptfos.unios.hr/cjfst/

Original scientific paper

DOI: 10.17508/CJFST.2018.10.2.08

Supercritical CO_2 extraction of oil from rose hips (*Rosa canina* L.) and cornelian cherry (*Cornus mas* L.) seeds

MARTINA JAKOVLJEVIĆ[1*], TIHOMIR MOSLAVAC[1], MATE BILIĆ[1], KRUNOSLAV ALADIĆ[2], FILIP BAKULA[3], STELA JOKIĆ[1]

[1]*Josip Juraj Strossmayer University of Osijek, Faculty of Food Technology Osijek, Franje Kuhača 20, 31000 Osijek, Croatia*
[2]*Croatian Veterinary Institute, Branch - Veterinary Institute Vinkovci, Josipa Kozarca 24, 32100 Vinkovci, Croatia*
[3]*University of Mostar, Faculty of Agronomy and Food Technology, Biskupa Ĉule bb,88000 Mostar, Bosnia and Herzegovina*

ARTICLE INFO

Article history:
Received: February 16, 2018
Accepted: April 14, 2018

Keywords:
Rosa canina,
Cornus mas,
supercritical CO2 extraction, oil, response surface methodology

ABSTRACT

Rose hips (*Rosa canina* L.) and Cornelian cherry (*Cornus mas* L.) seeds are waste products from the manufacture of juice, syrup, puree, jams or wines and as such, they contain significant amount of oil. Special emphasis in the last few decades is given to "green" supercritical CO_2 (SC-CO_2) extraction technique which is environmentally friendly and enables better extraction yield, better quality of the extract, and better resource saving. In this study the SC-CO_2 extraction was used to obtain oil from two different sources: rose hips and cornelian cherry seeds. The aim was to investigate the influence of different extraction parameters, pressure (119-331 bar) and temperature (36-64 °C) on: (1) oil yield; (2) peroxide value; (3) and the determination of the optimal extraction conditions by response surface methodology (RSM) using Central composite rotatable design (CCRD). Fatty acid composition of obtained oils was determined by gas chromatography and mass spectrometry (GC-MS). Oil yield of rose hip seeds varied between 3.26-7.75% while peroxide number was between 4.70-29.69 mmol O_2/kg, depending on applied extraction conditions. As for cornelian cherry seed oil, oil yield was 2.35-5.18% and the peroxide number of oil, depending on the extraction parameters used, was 0.55-7.36 mmol O_2/kg. At 300 bar and 40 °C, rose hip seed oil mainly contained linoleic acid (52.45%) followed by linolenic acid (20.55%), oleic acid (19.81%), palmitic acid (3.64%), stearic acid (2.34%) and arachidic acid (0.95%) while cornelian cherry seed oil contained linoleic acid (65.73%), oleic acid (23.69%), palmitic acid (8.05%), stearic acid (1.92%), erucic acid (0.48%) and arachidic acid (0.13%).

Introduction

Rose hips (*Rosa canina* L.) are fruits belonging to the Rosaceae family spread over the subtropic regions of Europe, Asia, the Middle East and North America (Nilsson, 1997; Chrubasik et al., 2008). Rose hips are not only a valuable source of many pharmacologically active compounds, but they also contain nutrients, including high quality seed fatty oil (Adamczak et al., 2011). Rose hips seeds (achines) contain from 4.9% to 17.82% of oil and are a waste product from the manufacture of rose hip juice or syrup, (Zlatanov, 1999; Szentmihalyi et al., 2002; Özcan, 2004) making that oil one of the greatest ways to use waste from the food industry due to its high content of unsaturated fatty acids, such as linoleic, α-linolenic and oleic acid (Szentmihalyi et al., 2002; Özcan, 2004; IuriIlyasoğlu, 2014). Because of its composition, this oil exhibits an effect on improving lipid metabolism, possible anticancer effect, as well as a positive effect on skin diseases including dermatoses, ulcers (Chrubasik et al., 2006) and the effects on skin aging (Datta et al., 2011; Fujii et al., 2011; Korać and Khambholja, 2011; Schagen et al., 2012; Binic et al., 2013; Phetcharat et al., 2015).

*Corresponding author E-mail: mjakovljevic@ptfos.hr

Cornelian cherry (*Cornus mas* L.) is a plant from family Cornaceae, which grows in the temperate regions of the Northern Hemisphere, Peru and in the regions of Europe, Asia, Iran, Turkey and Armenia (Rop et al., 2010). Cornelian cherry seeds, waste products from raw material processed into products such as puree, jams, juices or wines, are a substantial source of unsaturated fatty acids. The most abundant is linoleic, which is followed by oleic, palmitic and linolenic acid. Oil content in the seeds varied from 4.45% to 7.94% (Vidrih et al., 2012).

The yield and the quality of the obtained oil depend on the extraction technique, the type of solvent as well as on the working conditions. SC-CO_2 extraction appears as an alternative method for the oil production in comparison to the conventional methods such as extraction with organic solvents and cold pressing due to the environmental benefits and better oil quality compared to the present traditional methods of extraction with organic solvents. Also, it provides better extraction yields compared to mechanical pressing (Jokić et al., 2015). CO_2 is an excellent solvent in supercritical state since it is safe, non-toxic and easily removed from the sample (Laroze et al., 2010). Another advantage of SC-CO_2 is the use of lower temperatures and the protection of bioactive components from thermal degradation (El Asbahani, 2015).

Oil quality can be determined by various parameters, including the peroxide number representing the degree of oxidative degradation of vegetable oils. The peroxide number of oils is determined by standard method (ISO 3960:1998). The peroxide number is influenced by storage conditions, such as light and temperature. By increasing the temperature and exposure to the light, the peroxide number gets higher (Abramovič and Abram, 2005; Popa, 2017). Likewise, the degree of unsaturation of the fatty acids present in the oil affects the peroxide number as well as the presence of metals and other components that can catalyze the oxidation process and oil processing (Choe, 2006).

In this context, the aim of this study was to investigate the influence of the most important SC-CO_2 extraction parameters, pressure (119-331 bar) and temperature (36-64 °C) on: oil yield and peroxide value of rose hips and cornelian cherry seed oils, respectively. Furthermore, the optimal extraction conditions were determined by response surface methodology (RSM) using Central composite rotatable design (CCRD) for both oils.

Materials and methods

Materials

Rose hips (*Rosa canina* L.) and cornelian cherry (*Cornus mas* L.) seeds were obtained from family farm owned by Antonija Zelenika (Velika, Croatia). The purity of CO_2 used for extraction was 99.97% (w/w) (Messer, Osijek, Croatia). Industry FAME mix 37 standard for fatty acids analysis was purchased from Restek (USA). All other solvents were of analytical grade and purchased from J.T. Baker (PA, USA).

Experimental procedure

The determination of initial oil and moisture content

The initial oil content in seed samples was measured by automatic extraction systems Soxterm by Gerdhart with *n*-hexane (Aladić et al., 2014). Moisture content of the seed samples was determined according to AOAC Official Method 925.40 (2000). The measurements were done in duplicate.

Supercritical CO_2 (SC-CO_2) extraction

The experiment was performed in SC-CO_2 system explained in detail elsewhere (Jokić et al., 2015). The grounded dried rose hips or cornelian cherry seeds of 100 g were placed into extractor vessel. The oil was collected in previously weighed glass tubes. The amount of oil obtained after previously determined period of time was established by weight, using a balance with a precision of ±0.0001 g. Separator conditions were 15 bar and 25 °C.

The extraction was performed at different extraction conditions determined by CCRD. The extraction time of 90 minutes and CO_2 mass flow rate of 2 kg/h were kept constant during experiments. The extracts were kept at 4-6 °C for further analyses.

Experimental design

Central composite rotatable design (CCRD), explained in detail by Bas & Boyaci (2007), was used for determining optimal process conditions of pressure and temperature for SC-CO_2 extraction of oil from rose hips and cornelian cherry seeds. Extraction pressure (X_1) and temperature (X_2) were independent variables studied to optimize the extraction process in terms of getting higher oil yield and lower peroxide value in the obtained oils. Investigated factors and levels tested were reported in Table 1.

Table 1. The uncoded and coded levels of independent variables used in the RSM design

Independent variables	Symbols	Levels				
		-1. 414	-1	0	+1	1. 414
Pressure (bar)	X_1	119	150	225	300	331
Temperature (°C)	X_2	36	40	50	60	64

Experimental data were fitted with second order response surface model with the following form:

$$y = \beta_0 + \sum_{j=1}^{k} \beta_j X_j + \sum_{j=1}^{k} \beta_{jj} X_j^2 + \sum_{i<j}\sum \beta_{ij} X_i X_j \quad (1)$$

where y stands for investigated responses (oil yield and peroxide value), β_0, β_j, β_{jj}, β_{ij} are constant coefficients of intercept, linear, quadratic, and interaction terms, respectively; X_i and X_j are coded independent variables (extraction pressure and temperature). The analysis was performed using commercial software *Design-Expert*® (ver. 9, Stat-Ease Inc., USA). The analysis of variance (ANOVA) was also used to evaluate the quality of the fitted model. The test of statistical difference was based on the total error criteria with a confidence level of 95.0%.

Oil quality

Free fatty acids, iodine value and saponification value were determined according to AOAC Official Methods 940.28, 920.185 and 920.160 (1999). Peroxide value of oil samples was determined according to ISO 3960 (1998) and was expressed as mmol O_2/kg of oil. Insoluble impurities were determined according to ISO 663 (1992). All these determinations were carried out in triplicate.

The determination of fatty acid composition

The preparation of fatty acid (FA) methyl esters was carried out according to HRN EN ISO 12966-2:2011 standard by saponification of glycerides with NaOH in methanol. After that, the soaps were converted into FA methyl esters by reaction with BF_3 methanol complex.
Prepared FA methyl esters were analyzed by gas chromatography according to HRN EN ISO 12966-1:2015. Gas chromatograph 7890B (Agilent Technologies, Lake Forest, USA) with a capillary column: Rtx®-2560 (biscyanopropyl polysiloxane) 100 m long with a diameter of 0.25 mm and the thickness of the stationary phase 0.20 microns (Restek, USA), a splitless injector (temperature 225 °C) and a flame-ionization detector (temperature 250 °C) were used with a sample volume of 1 µL. The starting temperature was 100 °C with holding time for 4 minutes. The oven temperature was increased with a rate of 3 °C/min to 240 °C/min, holding for 11 minutes. The carrier gas was nitrogen (99.9999%) at constant flow rate of 1.2 mL/min. The hydrogen flow was 30 mL/min, air flow was 250 mL/min, and the makeup gas flow (nitrogen) was 45 mL/min. FA methyl esters in samples were identified by comparison with retention times of 37 FA methyl ester standard at the same conditions. Prior to standard and sample analysis, certified reference material (CRM) was prepared and analysed at the same conditions. The results were expressed as percentage (%) of individual fatty acids to total fatty acids. The detection limit was 0.01%. The analysis was conducted in two replications.

Results and discussion

Rose hip and cornelian cherry seed oils were obtained by SC-CO_2 extraction using different process parameters (pressure and temperature). The oil yield and peroxide values of obtained oils were monitored after different extraction experiments (Table 2) and the process was optimized using RSM. The yield of rose hip seed oil varied depending on the parameters used in the range of 3.27-7.75%, with the lowest yield at 119 bar and 50 °C and the highest in the experiments performed at 300 bar and 60 °C. In work by del Valle et al. (2000) the yield of rose hip seed oil ranged from 4.65±0.13% at a pressure of 400 bar, 40 °C and 90 minutes to 7.09±0.12% at 400 bar, 60°C and after 270 min. Machmudah et al. (2007) showed that yield of rose hip seed oil depends on the parameters used, primarily on the pressure, and can range from 1.827% to 15.93%. As far as cornelian cherry seed oil is concerned, the yield was in the range of 2.35-5.18% depending on the parameters used, with the lowest yield at 119 bar and 50 °C and the highest at 300 bar and 60 °C.
Primary oxidation processes in the oil mainly form hydroperoxides, which are measured by the peroxide value. In general, the lower the peroxide value, the better the quality of the oil (Frankel, 2005). In this study, the peroxide value for rose hip oil varied from 4.70-29.69 mmol O_2/kg and for cornelian cherry seed oils from 0.55-7.36 mmol O_2/kg. The value of the peroxide number was significantly lower in the sample of cornelian cherry in all experiments since the plant was freshly harvested which affects the final result of the peroxide number in the obtained oil.

Table 2. The experimental design and data for the response surface analysis

Run	Pressure (bar)	Temperature (°C)	*Rose hips*		*Cornelian cherry seed*	
			Oil yield (%)	Peroxide value (mmol O_2/kg)	Oil yield (%)	Peroxide value (mmol O_2/kg)
1	225	50	6.88	21.19	4.92	4.45
2	225	36	6.09	26.34	4.44	7.36
3	119	50	3.27	4.70	2.35	0.55
4	331	50	5.97	31.86	5.13	5.79
5	225	50	6.42	21.35	4.16	4.30
6	225	64	7.19	9.83	4.92	5.91
7	225	50	6.67	21.76	4.95	4.32
8	225	50	5.95	25.25	4.99	4.77
9	150	40	4.52	11.62	2.85	2.68
10	225	50	6.87	21.26	4.94	4.40
11	150	60	4.35	4.95	3.51	2.08
12	300	60	7.75	29.69	5.18	5.10
13	300	40	5.47	25.00	4.64	5.73

Extraction time: 90 min; CO_2 flow rate: 2 kg/h

Table 3. Corresponding *p*-values for selected response variable for each obtained coefficients

Response	**Term***				
Rose hip oil	X_1	X_2	X_1^2	X_2^2	X_1X_2
Oil yield	< 0.0001	0.0044	< 0.0001	<0.9040	0.0059
Peroxide value	< 0.0001	0.0250	< 0.1326	0.1177	0.1144
Cornelian cherry oil					
Oil yield	< 0.0001	0.0622	0.0015	0.4146	0.8457
Peroxide value	< 0.0001	0.0920	0.0055	0.0073	0.9806

*X_1: extraction pressure; X_2: temperature; $p < 0.01$ highly significant; $0.01 \leq p < 0.05$ significant; $p \geq 0.05$ not significant

The proportion of unsaturated fatty acids in oil can also affect the peroxide number since their oxidation can occur already in the seeds as well as in the process of separating seeds from the rest of the plant (Gustinelli et al., 2018). Nonetheless, other authors like Concha et al. (2006) showed that the peroxide number of rose hip oil was in the range from 0.3 mmol O_2/kg (organic solvent) to 1.7 mmol O_2/kg (cold pressing) while Grajzer et al. (2015) showed that peroxide number was 1.2±0.0 and 2.1±0.11 mmol O_2/kg, depending on the type of sample. Unfortunately, we did not find the data for the peroxide value for cornelian cherry seed oil from other works.

Table 3 shows the regression coefficients obtained by fitting experimental data to the second-order response models for investigated responses. The coefficients are related to coded variables. The first-order term of pressure (X_1) had a statistically significant effect ($p < 0.0001$) on the oil yield and peroxide value of both obtained oils. The first-order term of temperature (X_2) had a significant effect only in the case of rose hip oil, while in the case of cornelian cherry oil it did not show statistically significant effect on oil yield and peroxide value ($p > 0.05$). The second-order term of pressure (X_1^2) had a significant effect ($p < 0.05$) on both oil yields. The second-order term of temperature (X_2^2) had a significant effect only on peroxide value of cornelian cherry seed oil. The interactions between the extraction pressure and temperature had a significant effect only on rose hip oil yield.

The ANOVA results for the modelled responses are reported in Table 4 (*F*-test and probability). Joglekar and May (1987) suggested that for a good fit of a model, R^2 should be at least 0.80. In our study, the R^2 values for all investigated response variables were high. They varied from 0.9282 to 0.9642, indicating the adequacy of the applied regression models. The probability (*p*-value) of all regression models was below 0.05, which means that there was a statistically significant multiple regression relationship between the independent variables and the response variable. Also, the models had no significant lack of fit ($p > 0.05$). The best results were obtained for oil yield of rose hips (R^2 was 0.964 and *p*-value < 0.0001).

The best way to express the effect of SC-CO_2 parameters on oil recovery and peroxide value of both investigated oils within the investigated experimental range was to generate response surfaces of the model (Figs. 1–2). Fig. 1. shows the extraction yield and peroxide values of rose hip oil as a function of extraction pressure and temperature. The amount of obtained rose hip oil significantly decreases with the higher pressures up to 250 bar, while further increase shows slightly decrease in oil yield. Fig. 2. shows the extraction yield and peroxide values of rose hip oil as a function of extraction pressure and temperature. It can be seen that the oil yield and peroxide value is significantly influenced by increasing extraction pressure.

Temperature did not show any significant influence. According to Gustinelli et al. (2018) this can be explained by increased solubility of peroxide compounds with pressure increase. This can be seen in the experiments under the same conditions, where all the oils obtained in the experiments (other than the run 8) showed the same value of the peroxide number. Although extraction over 90 min at a higher temperature may affect the rate of lipid oxidation, it is important to know that during the SC-CO_2 process the sample does not come into contact with oxygen that limits the lipid oxidation process. For a full understanding of the solubility component impact, apart from studying SC-CO_2 parameters, knowledge of the properties and interaction of the components of a particular extracted material is required.

The final goal of RSM is the process optimization. Thus, the developed models can be used for simulation and optimization. Optimization is an essential tool in food engineering for the efficient operation of different processes to yield a highly acceptable product. In this study the following optimization conditions were proposed for calculations: the maximum oil yield and the minimum peroxide value. The goal of this research was to find the best process parameters for SC-CO_2 extraction for both oils separately. By applying desirability function method (Cojocaru et al., 2009), the optimum extraction conditions for rosehip oil were obtained at the pressure of 225 bar and the temperature of 64 °C, while for cornelian cherry seed oil it was at 300 bar and the temperature of 60 °C. Under these optimal conditions, the oil yield of rose hips was calculated to be 7.44% and peroxide value 9.13 mmol O_2/kg, which is in very close agreement with obtained experimental data (run 6, Table 2). In the case of cornelian cherry seeds, the oil yield was calculated to be 5.22% and peroxide value 4.96 mmol O_2/kg, which is very close to obtained experimental data (run 12, Table 2). Furthermore, in obtained oils the fatty acid profile and basic quality parameters of oil were determined. Both oils contain unsaturated fatty acids (Table 5) whose oxidation can occur already in the seeds as well as in the process of separating seeds from the rest of the plant affecting the peroxide number (Gustinelli et al., 2018). The results of fatty acid profile obtained for rose hip oil obtained by SC-CO_2 extraction were similar to the results of several other studies. Machmudah et al. (2007) determined the composition of fatty acids of rose hip oil obtained at 300 bar and 80 °C which included linoleic (49.33%) and linolenic acid (37.84%) followed by palmitic (4.17%) and stearic acid (2.85%). Illes et al. (1997) showed the composition of fatty acids of rose hip oil obtained at 250 bar and 35 °C, which included linoleic acid (53.0%) as most abundant, followed by linolenic acid (23.7%), oleic acid (16.7%), palmitic acid (3.5%), stearic acid (2.9%) and arachinic acid (0.1%). del Valle et al. (2000) showed that the most common fatty acids in obtained oil at 300 bar and 40 °C were linoleic acid (43.90%), linolenic acid (35.11%), oleic acid (14.20%), palmitic acid (3.71%), and stearic acid (1.70%).

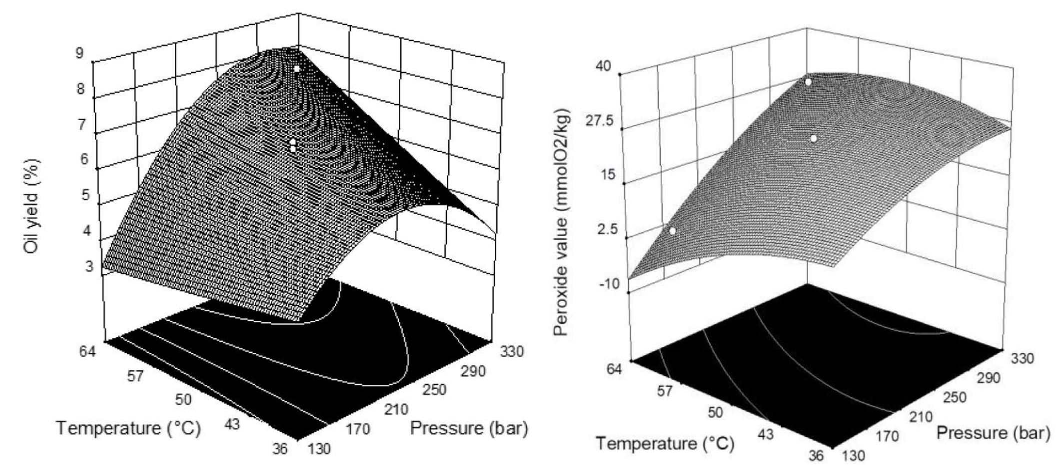

Fig. 1. Three-dimensional plot for obtained extraction yield and peroxide values of rose hip oil as a function of extraction pressure and temperature

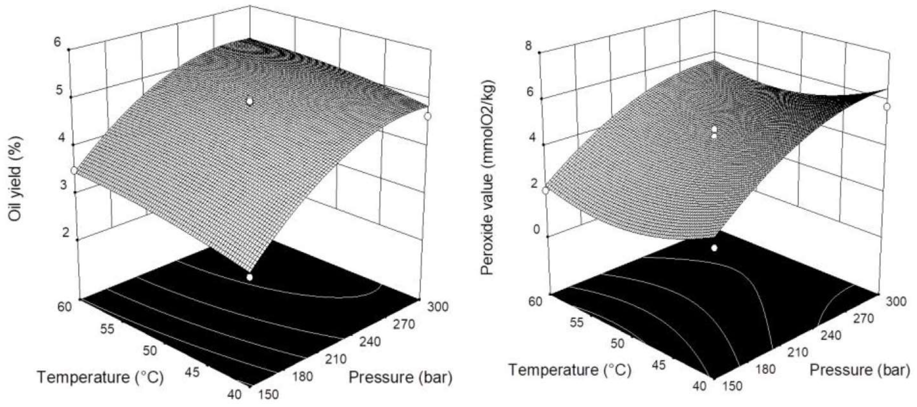

Fig. 2. Three-dimensional plot for obtained extraction yield and peroxide values of cornelian cherry seed oil as a function of extraction pressure and temperature

Table 4. Analysis of variance (ANOVA) of the modelled responses

Source	Sum of squares	Degree of freedom	Mean square	F-value	*p*-value
Rose hip oil					
Oil yield					
The recovery					
Model	18.58	5	3.72	37.66	< 0.0001
Residual	0.69	7	0.09		
Lack of fit	0.09	3	0.03	0.21	0.8868
Pure error	0.60	4	0.15		
Total	19.27	12			
R^2 = 0.9642					
Peroxide value					
The recovery					
Model	897.93	5	179.59	18.09	0.0007
Residual	69.47	7	9.92		
Lack of fit	57.36	3	19.12	6.31	0.0536
Pure error	12.12	4	3.03		
Total	967.40	12			
R^2 = 0.9282					
Cornelian cherry oil					
Oil yield					
The recovery					
Model	9.54	5	1.91	21.48	0.0004
Residual	0.62	7	0.089		
Lack of fit	0.12	3	0.039	0.31	0.8205
Pure error	0.51	4	0.13		
Total	10.17	12			
R^2 = 0.9388					
Peroxide value					
The recovery					
Model	36.07	5	7.21	20.42	0.0005
Residual	2.47	7	0.35		
Lack of fit	2.33	3	0.78	21.52	0.0063
Pure error	0.14	4	30.036		
Total	38.55	12			
R^2 = 0.9358					

As far as we know, there are no works on SC-CO_2 extraction of cornelian cherry seed oil, so the composition of obtained oil can not be compared to the oil obtained by the supercritical extraction of other authors. It can only be compared to the composition of the oil obtained using the Soxhlet apparatus. For example, Vidrih et al. (2012) examined the composition in stones of various cornelian cherry genotypes from Bosnia and Herzegovina and showed that they contained 4.91 to 7.94% of the fat extracted in the Soxhlet apparatus.

Table 5. Fatty acids composition of SC-CO_2 rose hip and cornelian cherry seed oils

Fatty acids	***Rose hip oil****	***Cornelian cherry oil****
Palmitic acid (%)	3.64	8.05
Stearic acid (%)	2.34	1.92
Oleic acid (%)	19.81	23.69
Linoleic acid (%)	52.45	65.73
Linolenic acid (%)	20.55	-
Arachidic acid (%)	0.95	0.13
Erucic acid (%)	-	0.48

* SC-CO_2 oils obtained at 300 bar and 40°C

Table 6. Quality parameters of of SC-CO_2 rose hip and cornelian cherry seed oils

Properties	***Rose hip oil***	***Cornelian cherry oil***
Free fatty acids (as % oleic acid)	3.06	2.43
Insoluble impurities (%)	0.71	-
Moisture content (%)	7.34	15.68
Iodine value (g iodine/100 g oil)	146.94	104.84
Saponification value (mg KOH/g)	194.64	146.45

The composition of fat in stones included mostly linoleic acid (64.8-72.2%), then oleic (15.5-22.9%), palmitic (7.3-8.1%), stearic (2.0-2.9%), linolenic (1.5-1.6%) and arachidic acid (0.3-1.5%). Kucharska et al. (2009) investigated cornelian cherry samples from Poland, and showed that the seeds had 0.32-3.57% of oils containing linoleic acid (70.7-75.0%), oleic acid (15.0-16.7%), stearic acid (3.5-6.2%), palmitic acid (3.5-4.6%) and linolenic acid (1.3-2.1%).

Using SC-CO_2 extraction, it is possible to extract almost 100% of oil present in rose hip seeds and cornellian cherry containing a high content of polyunsaturated fatty acids. According to the results in Table 5, together with all other sources mentioned, rose hip oil is rich in linoleic and linolenic acid that are essential fatty acids with many positive health effects in the body, and most of all in the prevention of cardiovascular disorders (Connor, 1999; Das 2000; Djoussé et al. 2001, 2003). The above-mentioned linolenic and linoleic acid are the precursors of omega-3 and omega-6 fatty acids whose proper intake is important not only in the prevention of chronic cardiovascular diseases but also in brain-mediated functions (Yehuda, 2003). Oleic acid, an unsaturated fatty acid present in both extracted oils, which in view of its beneficial effects on health (the reduction of blood pressure) contributes to the total nutritional quality of the produced oil (Terés et al., 2008). The absence of erucid acid is noticable in rose hip oil as well as low percentage of erucid acid in cornelian cherry oil which is positive since it is considered to be an anti-nutritional component (Somerville 1993; Carlson et al. 1997; Gandhi et al. 2009).

The quality parameters specified in this study for both oils are listed in Table 6. Since investigated oils in this study are not widely used, especially in nutrition, the requirements are not specified in the Ordinance on Edible Oils and Fats NN 41/2012. The iodine value for rose hip oil was 146.94, which is not consistent with the value of 179.0 presented by Concha et al. (2006) or value of 175.00 presented by del Valle et al. (2000). In addition, although notably less, the value of the saponification number also varies, so in our case this value was 194.64 mg KOH/g, while in paper by Concha et al. (2006) and del Valle et al. (2000) value was 187.2 and 189.3 mg KOH/g, respectively.

Conclusion

RSM has been successfully applied to optimize the oil extraction process from rose hips and cornelian cherry seeds using SC-CO_2. According to ANOVA it is apparent that the extraction pressure had the greatest influence on the oil yield, because increased pressure (at constant temperature) results in an increase in the density of the SC-CO_2 and thus increases the efficiency of the extraction process. The temperature did not have a statistically significant effect on oil yield. The extraction parameters have a statistically significant effect on the peroxide number, so it is important to select the parameters that will produce the oil with a lower peroxide number as it is a sign of oxidative degradation. By using SC-CO_2 extraction, the oil can be completely extracted from raw material, which is of great importance in industrial processes.

Rose hip oil and cornelian cherry seed oil proves to be a valuble source of polyunsaturated fatty acids such as linolenic and linoleic acid. According to other valuable information from literature that rose hips oil exhibits an effect on improving lipid metabolism, possible anticancer effect, and positive effect on skin diseases including dermatoses, ulcers and the effects of skin aging, and the fact that cornelian cherry seed oil shows the possibility of recovering and regenerating external and internal epidermal tissues and possesses significant antimicrobial activity, the utilisation of rose hip seeds and cornelian cherry seed, treated generally as waste products, may enhance the profitability of cultivation.

Acknowledgments

The authors are grateful to the Josip Juraj Strossmayer University of Osijek, Republic of Croatia for financial support.

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