JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY

Article

pubs.acs.org/JAFC

Effect of Deodorization of Camelina (*Camelina sativa*) Oil on Its Phenolic Content and the Radical Scavenging Effectiveness of Its Extracts

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ABSTRACT: The influence of deodorization parameters (temperature (T), steam flow (S), time (t)) on the phenolic content and radical scavenging effectiveness (RSE) of methanolic extracts of camelina oil was investigated and analyzed by response-surface methodology (RSM). The phenolic content can be considered to be a linear function of all three parameters. A positive linear relationship between the content of phenolic compounds in deodorized oils and RSE was observed. Deodorization at 210 °C with a steam flow of 3 mL/h for 90 min resulted in the best preservation of phenolics, amounting to 29.9 mg/kg. The lowest reduction from RSE of 12.4 μM Trolox equivalents (TE)/g oil for the crude oil was observed for oil treated at 195 °C and 18 mL/h for 60 min with RSE of 10.1 μM TE/g oil. The lack of correlation between RSE or total phenolic content and oxidative stability (OS) of the deodorized oils suggests that antioxidants in scavenging radicals react by different mechanisms, depending on radical type and reaction medium.

KEYWORDS: *camelina oil, Camelina sativa, deodorization, polyphenols, radical scavenging effectiveness*

■ INTRODUCTION

Camelina sativa is an important oilseed crop, belonging to the Brassicaceae family. In recent years this crop has received great attention because of the nutritional properties of its oil and its suitability for use in non-nutritional applications such as biofuel. Camelina meal due to its high content of proteins and carbohydrates and low levels of glucosinolates[1,2] can be used as feedstock. Camelina oil is considered to be a high value added product due to its considerable content of omega-3 α-linolenic acid $C_{18:3n\text{-}3}$ (30−40%) and low content of eruic acid $C_{22:1n\text{-}9}$ (about 3%). The presence of tocopherols (approximately 700 mg/kg) and phenolic compounds (approximately 100 mg/kg as chlorogenic acid) also makes it more stable toward oxidation than other highly unsaturated oils such as flax oil.[3−5] Camelina oil has an attractive yellow color, a mustard-like taste, and a characteristic odor. The flavor and odor make its acceptance difficult among European and North American consumers, mainly because of their different expectations of the organoleptic properties of vegetable oils.[6] Processing techniques such as refining can produce oils which are flavorless, odorless, and with reduced acidity.[7]

Phenolic compounds are among the most widely distributed secondary plant metabolites and are generally involved in defense against infection and injury. In foods, phenolic compounds may contribute to taste, aroma, color, and oxidative stability.[8] In addition, they have been associated with health benefits against the development of cancers, cardiovascular diseases, diabetes, osteoporosis, and neurodegenerative diseases.[9] The antioxidant activity of phenolic compounds in plants is mainly due to their redox properties and chemical structures, which can play important roles in scavenging free radicals, chelating transition metals, and quenching singlet and triplet oxygen molecules.[10] A recent publication[11] showed that after oil pressing, most of the phenolic compounds remain in the seed residues. The compounds successfully identified in the methanolic extract of camelina oil were ellagic acid, *p*-hydroxybenzoic acid, sinapic acid, salicylic acid, catechin, and quercetin.[11] With its antioxidant properties revealed in the same study, especially its great chelating ability and significant protective effect against oxidation of the emulsion, camelina oil thus appears to provide a potentially useful source of antioxidants.

During refining, unfortunately, the content of valuable minor compounds, tocopherols, sterols, and phenolic compounds, is reduced. Different studies on vegetable oils have shown that the phenol concentration decreases with increasing degree of refinement, where neutralization and bleaching result in major removal of these minor compounds.[12−16] On the contrary, water degumming, a process for removing phospholipids from oil, does not significantly affect the content of total polyphenols,[13,16] whereas after mild deodorization, oil samples with a considerable residual amount of polyphenols (50−75% as compared before deodorization) were retained, resulting in a higher oxidative stability than that of fully refined oils.[16] Deodorization is a physical process comprised holding and steam refining of oil at elevated temperatures and low absolute pressures to remove unwanted odoriferous compounds, namely, various oxidation products.[17] During deodorization, phenolics, depending on their volatilities, are partly evaporated from the oil and concentrate in distillate steam as the so-called deodorizer distillate. When optimizing operating conditions for

Received: March 5, 2013
Revised: August 6, 2013
Accepted: August 8, 2013
Published: August 8, 2013

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refining highly unsaturated camelina oil, it is important to find a compromise between the need to maximize the elimination of unwanted compounds and the desire to retain valuable compounds, thus improving the oxidative stability and retaining the nutritional value of the finished oil.

Recently, we conducted a detailed study on the optimization of the deodorization parameters, that is, temperature, steam flow, and time.[18,19] These studies, however, did not indicate what fraction of the polyphenols are removed/retained during deodorization of camelina oil. Therefore, in the present work an attempt has been made to quantify the changes in phenolic content and their antioxidant activity with respect to deodorization conditions. Response-surface methodology (RSM) was used for analyzing these experiments.

MATERIALS AND METHODS

Camelina Oil. Camelina (*Camelina sativa* (L.) Crantz) seeds were purchased from a certified organic seed dealer and cold pressed with a screw press. The oil was centrifuged (4200 rpm, 30 min). The degumming step was carried out for 30 min at a temperature of 70 °C and 100 rpm agitation, with addition of 3% water and 0.5% citric acid (30% w/v). Finally, the gums were separated by precipitation and decantation. The results of characterization of the degummed oil, as recently published,[18,19] were as follows: peroxide value = 1.6 mequiv/kg, *p*-anisidine value = 0.41, content of total tocopherols = 780 mg/kg.

Reagents and Solvents. Hexane, ethanol (96%), methanol (99.9%), and sodium carbonate were obtained from Merck (Darmstadt, Germany). Folin−Ciocalteu (FC) reagent, 2,2-diphenyl-1-picrylhydrazyl ($DPPH^{\bullet}$) reagent, and chlorogenic acid were purchased from Sigma-Aldrich GmbH (Steinheim, Germany). For preparation of solutions ultrapure water (Milli-Q, Millipore) was used.

Deodorization Process. Bench-scale deodorization of camelina oil was conducted in 2000 g batches. The deodorization apparatus has been previously described.[20] It consists of a 5 L deodorizer flask, a steam generator with the steam tube extending to the bottom of the deodorizer flask, a round-bottom fully insulated condenser flask with a 50 mm coldfinger containing ethanol, and a mechanical vacuum pump. First, the flow of steam was controlled by regulating the distance (d) between the 150 W heating body and the glass steam generator. The distances of 3, 18, 30, 42, and 46 cm correspond to steam flows of 8, 6, 4, 2, and 0 mL/h, respectively. The oil was then deaerated by setting the vacuum pump at a constant pressure of 5 mbar. Following that, the deaerated oil was heated to 85 °C and kept there for 10 min to evaporate residual water from the degumming process. Finally, the deaerated oil was heated to the desired T. At the end of the desired deodorization t, the deodorized oil was cooled. Once the deodorized oil reached 60 °C, nitrogen gas was introduced into the apparatus to induce a normal atmosphere. The experimental was designed as follows. A central composite design with three factors and five levels was chosen. The ranges for the parameters, namely, T (180−240 °C), S, that is, d (0−8 cm), and T (30−150 min), were selected to mimic the deodorization conditions that are usually applied in an industrial environment. This design generated a total of 14 experimental runs at different conditions and 6 runs at the central point (210 °C, 30 mL/h, and 90 min) using Design-Expert 7.0.0 (Stat-Ease, Inc., Minneapolis, MN, USA) software. All experiments were conducted in randomized order as suggested by the software to minimize the effect of unexplained variability in the observed response due to extraneous factors.

Extraction of Phenolic Compounds. Methanolic extracts of camelina oil were prepared according to the following procedure. The oil sample was first dissolved in hexane (1:10, w/v) and transferred to a separatory funnel. Then 80% (v/v) methanol was added to the oil at a ratio of 1:4 (w/v). After 5 min of shaking, the lower methanol layer was removed. The residue was then re-extracted under the same conditions twice more. The methanol phases were combined and concentrated in a rotary evaporator under vacuum at 40 °C. The dry residues were redissolved in absolute methanol.

Total Phenolic Content. The total content of phenolic compounds in camelina oil was determined spectrophotometrically.[21] An appropriately diluted extract or chlorogenic acid (as a calibration standard) was mixed with freshly prepared FC reagent, sodium carbonate solution (20%, w/v), and Milli-Q water. After 40 min, the absorbance was measured at 765 nm on a model 8453 Hewlett-Packard UV−visible spectrophotometer (Hewlett-Packard, Waldbronn, Germany) with a 1 cm cell. The results were expressed as milligrams of chlorogenic acid per kilogram of oil. The determination was conducted in triplicate, and results were averaged.

Radical Scavenging Effectiveness (RSE). The RSE of phenolic extracts was evaluated as their capability to scavenge free radicals by $DPPH^{\bullet}$ assay.[22] Briefly, 2.9 mL of a solution of $DPPH^{\bullet}$ (0.1 mM) in ethanol (96% (v/v)) was added to 0.1 mL of phenolic extract, and 30 min later, the absorbance was measured at 517 nm against ethanol (96%) as a blank ($A_{s\ 517}$). The absorbance of the control ($A_{c\ 517}$) was obtained by replacing the phenolic extract with 96% ethanol. A decrease in absorbance from $A_{c\ 517}$ to $A_{s\ 517}$ occurs when an antioxidant reacts with the $DPPH^{\bullet}$ radical. The RSE was expressed in micromolar Trolox equivalents (TE; calculated as Trolox concentration needed to reach the same effect as phenolic extract) per gram of oil. Triplicate analyses were run for each extract.

Statistical Analysis. The data were statistically analyzed and interpreted with RSM by statistical software as mentioned above. First- or second-order coefficients were generated by least-squares multiple regression analysis with hierarchical backward elimination at the 95% significance level ($p < 0.05$). Insignificant ($p > 0.05$) factors and interactions between factors were removed. Responses (total phenolic content, RSE) were fitted to the parameters (T, S, t) by multiple regression to produce a mathematical model:

$$Y = \beta_0 + \sum_{i=1}^{3} \beta_i X_i + \sum_{i=1}^{3} \beta_{ii} X_i^2 + \sum_{i=1}^{2} \sum_{j=i+1}^{3} \beta_{ij} X_i X_j \quad (1)$$

The fit of the model was evaluated according to the coefficient of determination (R^2) and analysis of variance (ANOVA). The main effect plot displays the predicted change in the response when parameters vary from their lowest to their highest level, whereas the third parameter in the design is set to its average value.

RESULTS

Main Effects on Total Phenolic Content. Table 1 shows the total phenolic content for the 20 experimental runs carried on under different deodorization conditions. All three deodorization parameters significantly affected the content of total phenolic compounds in deodorized oil. Only first-order parameters were significant, whereas those of second order and interactions between them did not influence the content of total phenolics, so the total phenolic content could be considered as a simple linear function of all three parameters ($R^2 = 0.68$) (eq 2; Figure 1). The actual coded values for S were the following: 46 mL/h = 0 cm, 42 mL/h = 2 cm, 30 mL/h = 4 cm, 18 mL/h = 6 cm, and 3 mL/h = 8 cm.

$$\text{total phenolic content} = -0.21T + 1.19d - 0.07t + 66.5 \quad (2)$$

In this study, the lowest reduction of total phenolic content was achieved in oil treated at 210 °C with S of 3 mL/h for 90 min (expt 12) (Figure 2). At the same T and t of deodorization, when S increased to 30 mL/h (expt 15−20), a more profound decrease of phenolic compounds was observed. A subsequent increase in deodorization T (240 °C) at unchanged t resulted in still greater losses of phenolic compounds (expt 10). It was found that shortening t to 30 min in comparison to oils deodorized for 90 min at the same conditions (210 °C, 30 mL/h) resulted in better preservation of phenolic compounds (expt 13).

Table 1. Deodorization Parameters and Experimental Results (Responses) for the Analysis of Samples in the RSM-Generated Experimental Design of Camelina Oil Deodorization[a]

expt	T (°C)	S (mL/h)	t (min)	total phenolic content (mg/kg)	phenolic concentration in extract (mg/mL)	RSE (μM TE/g)
	crude oil			40.7	0.41	12.4
1	195	42	60	22.1	0.22	8.6
2	225	42	60	22.5	0.23	6.3
3	195	18	60	27.9	0.28	10.1
4	225	18	60	18.0	0.18	7.2
5	195	42	120	21.5	0.22	9.4
6	225	42	120	6.0	0.06	6.6
7	195	18	120	24.5	0.25	9.1
8	225	18	120	16.5	0.17	7.3
9	180	30	90	26.6	0.27	9.8
10	240	30	90	18.2	0.18	6.5
11	210	46	90	18.2	0.18	8.6
12	210	3	90	29.9	0.30	9.1
13	210	30	30	25.1	0.25	8.6
14	210	30	150	19.0	0.19	7.4
15	210	30	90	22.8	0.23	9.1
16	210	30	90	21.2	0.21	9.4
17	210	30	90	21.1	0.21	9.7
18	210	30	90	22.1	0.22	7.5
19	210	30	90	22.5	0.23	8.2
20	210	30	90	20.9	0.21	7.6

[a]Abbreviations: T, temperature; S, steam flow; t, time; RSE, radical scavenging effectiveness of phenolic extracts. Total phenolic content is expressed as mg of chlorogenic acid per kg of oil. RSE is expressed in μM Trolox equivalents (TE) per g of oil.

Lower reduction of total phenolics was observed in oil treated at relatively mild conditions (180 °C, 30 mL/h, 90 min (expt 9) and 195 °C, 18 mL/h, 60 min (expt 3)). An increase in T to 225 °C at unchanged S and t (18 mL/h and 60 min, respectively) (expt 4) resulted in a profound lowering of phenolic content. On the other hand, an appreciably lower decrease was observed when T remained at 195 °C but S increased to 42 mL/h (expt 1).

The highest reduction of total phenolic content was obtained when the oil was subjected to the most severe deodorization conditions (225 °C, 42 mL/h, 120 min) (expt 6). Lowering S to 18 mL/h resulted in better preservation of phenolic compounds in the deodorized oil (expt 8). Lowering T from 225 to 195 °C with S remaining unchanged (expt 5) resulted in an even better preservation of phenolic compounds in the deodorized oil. A subsequent lowering of S to 18 mL/h resulted in a still greater preservation of phenolic compounds (expt 7). This is similar to that for 60 min of deodorization t (as described in the previous paragraph), when increased S had a lower impact on the loss of phenolic compounds than increased T.

As evident, around 50% of the original total phenolic content was retained when the deodorization parameters were adjusted to the central point (210 °C, 30 mL/h, 90 min) (expt 15−20). According to published results,[18,19] the same camelina oil deodorized under these conditions showed good organoleptic results and chemical properties (free fatty acids < 0.3%, trans fatty acids < 1%, peroxide value < 0.25 mequiv/kg), whereas its nutritional value was not significantly affected. Namely, it appears that the degradation of valuable polyunsaturated fatty acids, such as geometrical isomerization and polymerization, increases strongly at $T > 210$ °C.[19]

Main Effects on RSE. The RSE of the phenolic extract of the crude oil was higher than that of the extract from deodorized oils (Table 1). Temperature had a significant ($p < 0.05$, $R^2 = 0.64$) linear effect on the RSE, whereas none of the other parameters significantly affected the antioxidant activity of the extracts (eq 3).

$$\mathrm{RSE} = -0.068T + 22.7 \tag{3}$$

The lowest RSE was obtained by the use of higher T (Figure 1). Additionally, extracts obtained from oils deodorized at the highest T had only half of the RSE compared to the extract of the crude oil. This is explained by the fact that at higher T greater phenolics removal occurred. The lowest reduction of RSE from RSE = 12.4 μM TE/g of crude oil was observed for oil treated under relatively mild conditions (expt 3) with RSE = 10.1 μM TE/g. Oils deodorized at the central point (expt 15−20) on average showed RSE = 8.6 μM TE/g, whereas stronger deodorization conditions resulted in more notable reduction of the RSE of oils.

DISCUSSION

In our study RSM was used to predict the optimum deodorization conditions to achieve oil with minimum levels of undesirable compounds while maintaining high levels of the desirable components. RSM has become a popular tool in lipid studies for product development and process optimization.[23−25] It can provide a statistical mathematical model for prediction of a range of parameters necessary to achieve the desired responses. The major advantage of this technique is that it enables simultaneous evaluation and optimization of multiple components instead of evaluating single parameters one at a time.

As mentioned, the total phenolic content can be considered as a simple linear function of all three parameters (Figure 1). This is explained by the fact that at higher T, greater S, and longer deodorization t more polyphenols evaporate, thermally degrade, oxidize, or polymerize. For the oil obtained from rapeseed, which like camelina belongs to the Brassicaceae family, a reduction of 53% in phenolic content occurred when the oil was physically deodorized at 240 °C for 90 min.[16] Koski et al.[14] reported almost complete reduction of the initial phenolic concentration during the full oil processing (refining, bleaching, and deodorizing). As in rapeseed, the main phenolic compound in camelina oil is sinapic acid.[11] During heat treatment of camelina seed, vinylsyringol, another important antioxidant, is formed via decarboxylation of sinapic acid.[26] Koski et al.[14] and Wakamatsu et al.[27] succeeded in identifying 4-vinylsyringol in refined rapeseed oil, although its content decreased after each refining step and was absent in the highly purified refined oil. Spielmeyer et al.[28] did not find this decarboxylation derivative of sinapic acid in refined rapeseed oil. The presence of dimers of phenolic compounds is also possible. These arise from the phenolic radical coupling pathway that results in the formation of dimers, some of which are antioxidatively active but others are not. The transformation of 4-vinylsyringol to phenylindane (4-vinylsyringol dimer) that could take place during the oil deodorization process was proposed in accordance with recent observations.[29]

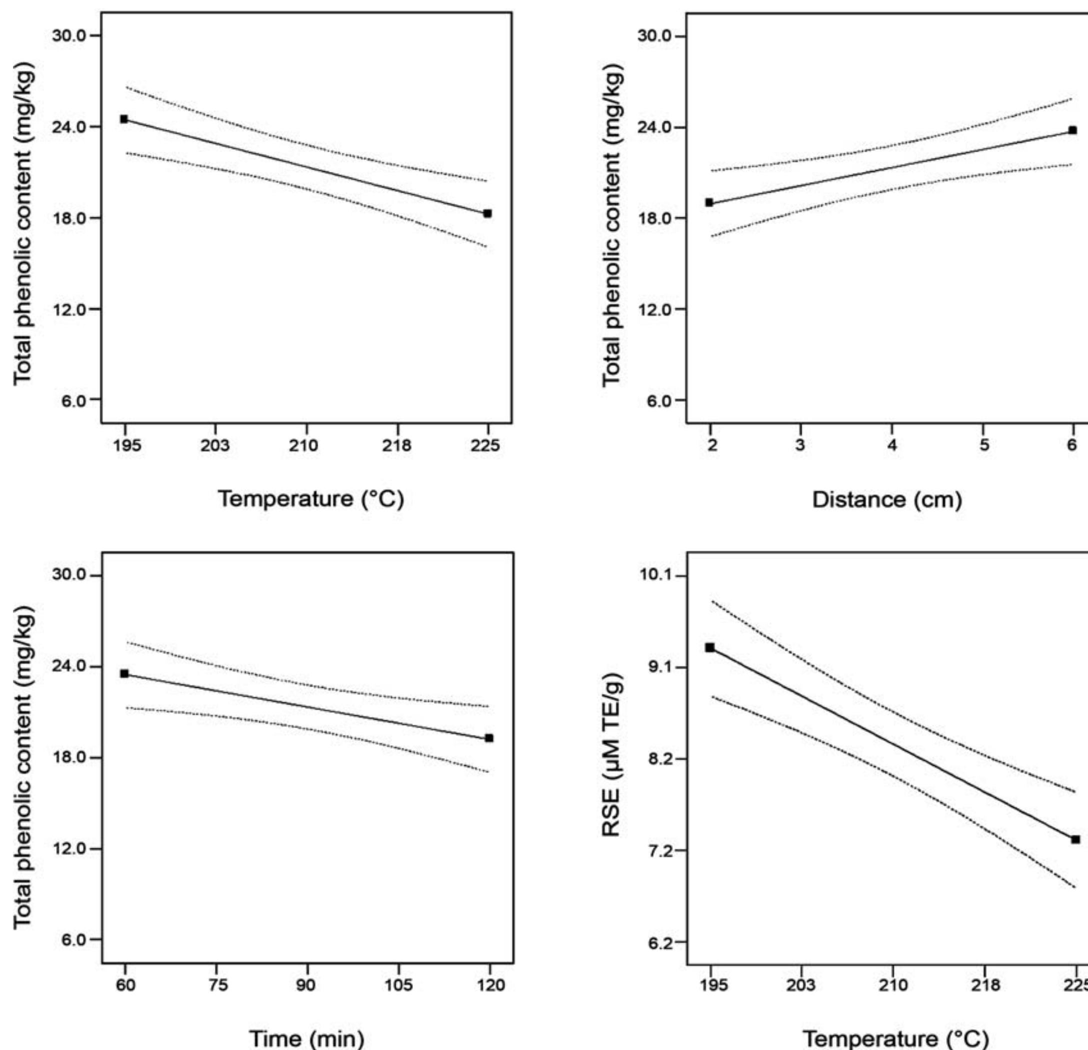

Figure 1. Main effects of deodorization parameters on total phenolic content and radical scavenging effectiveness (RSE) of phenolic extracts with 95% confidence intervals. The effects of each parameter when it is varied from a low to a high level and all other factors are kept at their averages are displayed.

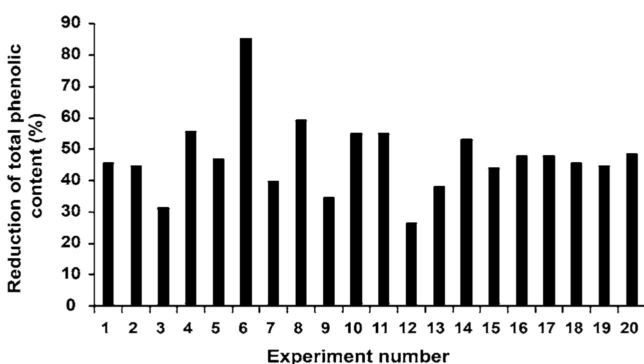

Figure 2. Reduction of total phenolic content in oils after deodorization (expressed as %).

We can observe a positive linear relationship between the content of total phenolics in deodorized oils and the RSE of their extracts with r amounting to 0.66. The correlations among responses were performed by linear regression analysis using the least-squares method. An even better correlation was observed when crude oil was included in the correlation analysis, with $r = 0.80$. This observation is expected because antioxidants are decomposed by deodorization. The correlation between oxidative stability (OS) of deodorized camelina oils and the RSE of their phenolic extracts was also investigated. The OS of oils was determined by Oxipress equipment and listed in the publication by Hrastar et al.[18] OS is defined as oxygen consumption evaluated by measuring changes in the pressure of the hermetically sealed 200 mL vessel (containing oil) filled with oxygen at an initial pressure of 5 bar and heated at 110 °C. We obtained a poor linear correlation between RSE and OS of the oils with $r = 0.35$, and no correlation ($r = 0.02$) when the crude oil was included in the statistical analysis. Furthermore, a very weak positive linear relationship ($r = 0.12$) was obtained between total phenolics and OS of deodorized oils. If crude oil was included in the statistical analysis, the data even showed a negative correlation. These observations reflect the fact that the presence of remaining phenols in deodorized oils alone might not contribute significantly to their OS. A better correlation of $r = 0.35$ was observed when the sum of antioxidants present in deodorized camelina oils, that is, the sum (on a molar basis) of total phenols and total tocopherols, was correlated with OS. The tocopherols were determined and listed as reported recently.[18] Again, a poorer correlation was

observed if crude oil was included in the statistical analysis (r = 0.11).

The lack of good correlations between RSE or total phenolics with OS of deodorized oils could be ascribed to various factors. RSE in fact represents the ability of phenolics extracted using 80% methanol to scavenge the DPPH$^\bullet$ radical as determined in homogeneous polar medium. It should be stressed that antioxidants react with DPPH$^\bullet$ radicals under conditions that are different from those occurring in the oil, where radical scavenging is based on a different reaction mechanism. In systems like the DPPH$^\bullet$ scavenging assay, due to possible interactions of phenolic compounds with the hydrogen bond accepting solvent, antioxidants scavenge radicals via electron transfer.[30] In oil, phenolics suppress oxidation and influence oxidative stability through reaction with alkylperoxyl radicals by the hydrogen atom transfer mechanism. The DPPH$^\bullet$ radical, in contrast to the alkylperoxyl radical, is a long-lived radical. Furthermore, the OS of the relatively complex oil system, besides the presence of antioxidants, depends on fatty acid composition and other minor constituents as well as various prooxidants.

It is well-known that the total content of antioxidants is not the most important parameter influencing the antioxidative potential of the system, but the presence of particular antioxidants and possible interactions between them might improve (synergistically) the oil's oxidative stability. This was confirmed for rapeseed oil, where sinapic acid, as in camelina oil, is the main phenolic compound; a significant synergistic action with tocopherol occurs in decreasing hydroperoxide formation in the oxidation of oil.[31] The antioxidant capacity of phenolic compounds decreases as lipid autoxidation increases. It has been shown that phenolic compounds are effective in the initial stage of autoxidation[32] and that tocopherols become more important in antioxidant activity when the hydroperoxide content reaches a critical level.[31] Due to its high content of polyunsaturated fatty acids camelina oil is highly susceptible to oxidation and formation of radicals. Phenolic compounds and tocopherols are potent antioxidants of camelina oil and contribute significantly to its greater OS, but the presence of free fatty acids and hydroperoxides accelerates the oxidation process and decreases the OS of the deodorized oil. During the deodorization, the concomitant formation of hydroperoxides, which decompose in a temperature-dependent manner to highly reactive radicals (act as promoters of oxidation by initiating a new oxidation chain reaction), formation of secondary oxidation products (most of them volatile compounds, which favor oxidation process), evaporation of volatiles, and decomposition of phenolics and tocopherol occur. As was reported,[18] in the range 195−215 °C the content of hydroperoxides decreased with increasing deodorization T, whereas with further increase in T the hydroperoxide content in deodorized oils increased. The same study revealed that all deodorization parameters have a negative effect on the content of free fatty acids, which are more prone to oxidation than those esterified in triacylglycerols. All of these observations suggest that the oxidative stability of oil deodorized at more rigorous conditions is a consequence of the successful removal of prooxidants and, to a lesser extent, a consequence of the antioxidative activity of residual antioxidants.

In conclusion, the main objective of our study was to design a refining process where undesired compounds (free fatty acids, peroxides, odiferous secondary oxidation products) would be successfully removed, thermal degradation of polyunsaturated fatty acids and formation of polymerized triacylglycerols minimized, and antioxidative compounds (phenolic compounds, tocopherols, and sterols) retained as much as possible. To the best of our knowledge this is the first time that the influence of deodorization on phenolics in camelina oil has been reported. The deodorization decreased the content of total phenolics in camelina oil and the radical scavenging ability of their extracts. By combining the results we can conclude that the most appropriate conditions for processing oils so that phenolics and the RSE of their extracts are maximally retained are a flow rate of 3−18 mL/h in the temperature range 195−210 °C and a deodorization time of 60−90 min. The differences in OS could not be fully elucidated either by analysis of the total phenolic content in deodorized oils or by evaluation of the RSE of their extracts; this could be explained by the fact that the environment influences the mechanism of reaction between phenolics and lipid radicals. Furthermore, our observations suggested that the content of antioxidants is not the main parameter influencing the oxidative stability of an oil but also possible interactions between them. Because the phenolic compounds in deodorized camelina oil remain to be identified and quantified, the influence of deodorization conditions on these compounds in deodorized oils will be further investigated.

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Author Contributions

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Funding

We are grateful to the Ministry of Education, Science and Sport of the Republic of Slovenia for financial support.

Notes

The authors declare no competing financial interest.

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