The objective of this study was to investigate the impact of seed storage time on the quality of cold-pressed sunflower oil. The quality and oxidative stability of oil was determined in samples of domestic varieties of sunflower hybrid, linoleic type seeds, obtained from fresh seeds and from seeds stored in silo cell for 6 and 12 months at temperature below 30°C and in good ventilation conditions. It was found that the longer storage time of seeds had a negative impact on many quality aspects of the oil, such as flavor, odor and aroma, primarily on the sensory profile. Chemical characteristics and oxidative stability of oil were also influenced by the storage time, which was confirmed by increased values of the acid value (AV) and peroxide value (PV) of the oil samples. Fresh seed oil had an AV of 0.49±0.01 mgKOH/g, while oils that were obtained from one-year old seeds had an AV of 1.95±0.02 mgKOH/g. Content of the primary oxidation products in the oil obtained by cold-pressing of the fresh seeds was 1.73±0.02 mmol/kg (measured as PV), and 2.22±0.07 mmol/kg in that from the seeds stored for 12 months. The anisidine value for the oil obtained from the seeds stored for 12 months was 0.86±0.04 (100A350nm).

KEY WORDS: sunflower seeds, cold-pressed oil, storage time, sensory quality, oxidative stability

INTRODUCTION

From a global perspective, edible, unrefined cold-pressed oils are getting more attention in the scope of today's healthy diet. Cold-pressed oils have high biological value, nutritive and chemical qualities, as well as a characteristic sensory profile that is appealing to consumers. A typical and well known representative of cold-pressed oils is olive oil, which has the longest tradition in cold-pressing oil processing. However, during the last decade, the assortment of edible cold-pressed oils has significantly increased using other available oilseeds, such as cold-pressed sunflower oil (1, 2, 3).

Besides the chemical composition and stability, quality characteristics of oils greatly depend on the production method. Since today's consumers have much higher expectations of food, which should be natural and wholesome, the oil manufacturing process...
must be designed in such a way that it will preserve the original raw material quality, including nutritional profile and its stability. At the same time, it is also important to reduce environmental pollution. The cold-pressing (also known as expeller-press) method for oil manufacturing meets all mentioned requirements (4, 5, 6).

Since the expeller-press (screw press) technology does not allow further oil quality adjustment, the main parameter that has an influence on the cold-pressed oil quality is the raw material. The most recent studies have shown that the major difference in the quality and oxidative stability of oils lies in the variability of the seeds used for the cold-pressing process. Therefore, the most significant factor in the manufacturing of cold-pressing oil is consistent and high-quality raw materials (7, 8, 9).

Oilseeds are usually not processed immediately upon harvesting, but are stored in silo cells for certain time (2, 5). Prolonged storage time of oilseeds has not only a negative impact on the quality and chemical composition, but also on the shelf-life of the cold-pressed oils (10). Perretti et al. (11) pointed out that cold-pressed oils obtained by the pressing of stored seeds have higher content of free fatty acids and primary products of oxidation and significantly lower oxidative stability, compared to the cold-pressed oils obtained from fresh seeds. Bax et al. (12) found cold-pressed oils obtained from pressing linoleic and oleic types of seeds stored for 8 months had a linear increase of acid and peroxide values. It was shown that the increased sunflower seeds storage time from 3 to 12 months caused an increase in the content of the secondary products of oxidation in cold-pressed oils, while the shelf-life decreased (8).

Sensory quality of the cold-pressed oils is the most important parameter that is used when cold-pressed oils are evaluated. Appearance, color, odor, flavor and aroma are characteristics that have the highest impact on the sensory evaluation and acceptance of the cold-pressed oils by consumers. Sensory evaluation is considered the best method for determining not only the oil quality, but also oil stability, which includes detection of compounds formed during the oxidative and other oil degradation processes (2, 5, 6, 9).

The primary objective of this study was to determine the impact of the seeds’ storage time on the sensory and chemical quality of the cold-pressed sunflower oil, that have the highest influence on the marketability of this type of oil. However, since this type of oil is relatively new, the published data of this kind of investigation is scarce and a comparison to our data is limited. The importance of this study also lies in the fact that sunflower oil is not only the most common cold-pressed oil present on our market, but is gradually expanding to the European region and therefore a better understanding of the seed storage time impact on the oil quality is very important.

**EXPERIMENTAL**

**Materials**

Sunflower seeds of the domestic hybrid variety, linoleic type, grown and harvested in the Erdevik’s vicinity, were used for this study. The fresh seeds were investigated immediately after harvesting and cleaning, while other seed samples were stored in the silo (14 tons capacity) under standard conditions below 30°C, controlled humidity and air circu-
lation during 6 and 12 months. Cold-pressed oils were manufactured from those seeds in a small oil processing facility using a screw press “Anton Fries” (Germany). The press had a capacity of 6-9 kg/h and worked at the screw speed of 35-45 rpm. Oil temperature at the exit was at 50-60°C. Cold-pressed oils were kept at room temperature (23°C) for 24 hrs in order to separate the sediment, after which the oil was decanted and filtered through filter paper. The obtained samples were kept in the refrigerator at 5°C.

Methods

Sensory evaluation of the samples was conducted by a three-member expert panel, using methodology as described by Dimić and Turkulov (13) and Premović (6). The scoring system using descriptive test procedures was used for the sensory evaluation and characterization of the oil quality as 0 point (unacceptable) to 5 point (optimal quality). The following parameters were evaluated: appearance, odor, flavor, aroma and color (14, 15). In addition, the sensory description of acceptable cold-pressed sunflower oil was provided.

Seed and oil quality was determined using the following analyses: acid value (AV) - ISO 660: 2000; peroxide value (PV) - ISO 3960: 2001; anisidin value (AnV) - ISO 6885: 2006). AV and PV were determined in the oil that was cold extracted (13).

RESULTS AND DISCUSSION

Sensory quality of the cold-pressed sunflower oils obtained from seeds stored for 0, 6 and 12 months

Sensory quality (scoring method). The most significant characteristics that distinguish cold-pressed and refined, solvent-extracted oils are a prominent flavor, odor and aroma of the raw materials (5, 16). The appearance (clarity), as well as color of the cold-pressed oils are also important sensory quality parameters as the consumers perform a visual assessment and make their purchase choice based on the sensory appeal (2, 6, 17).

The overall sensory quality of investigated cold-pressed oils was depicted using quantitative descriptive analysis (QDA) and the following parameters: appearance, odor, flavor, aroma and color (Figure 1). As shown in Figure 1, the oil samples differ in terms of the sensory quality. As expected, and which is in agreement with the literature data (2, 5), the oil obtained from the fresh seeds had the best sensory evaluation (the highest total score), as well as the maximum score for appearance and color.
Figure 1. Sensory quality of the cold-pressed sunflower oils obtained from the seeds stored for 0, 6 and 12 months

The obvious differences in the sensory evaluation are reflected in the overall scores, as well (Figure 2).

Figure 2. Overall sensory scores of the cold-pressed sunflower oils stored for 0, 6 and 12 months

*Sample No. 1 - oil obtained from the seeds stored for 0 months
Sample No. 2 - oil obtained from the seeds stored for 6 months
Sample No. 3 - oil obtained from the seeds stored for 12 months

It can be seen from Figure 2 that the overall sensory scores are between 15 (oil obtained from 12-month old seeds) to 21.25 points (oil obtained from fresh seeds). None of the samples achieved the highest possible score of 25 points, as all of them had some quality imperfections.
The lowest overall scores (Table 1) were given for the flavor (2.67) and aroma (3.08), while the high overall scores were obtained for appearance (4.67) and color (4.33). Odor was different among the oil samples (the average score was 3.50). The appearance (clarity) of oils was very similar and all samples were of high quality, regardless of the storage time of the seeds.

Table 1. The average score and the score range of the sensory evaluation values of the cold-pressed sunflower oils obtained from seeds stored up to 12 months

<table>
<thead>
<tr>
<th>Parametar</th>
<th>Average score (points)</th>
<th>Score range (points)</th>
<th>Maximum value* (points)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Odor</td>
<td>3.50</td>
<td>3-4</td>
<td>5</td>
</tr>
<tr>
<td>Flavor</td>
<td>2.67</td>
<td>1-4</td>
<td>5</td>
</tr>
<tr>
<td>Aroma</td>
<td>3.08</td>
<td>2-3.75</td>
<td>5</td>
</tr>
<tr>
<td>Appearance</td>
<td>4.67</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>Color</td>
<td>4.33</td>
<td>4-5</td>
<td>5</td>
</tr>
<tr>
<td>Overall sensory score</td>
<td>-</td>
<td>15-21.25</td>
<td>25</td>
</tr>
</tbody>
</table>

* maximum possible values according to the described methodology

Description of the characteristic sensory quality parameters. Cold-pressed oils must have a specific and pronounced aroma that is characteristic for the raw materials, without any presence of foreign odor, flavor or signs of rancidity (3, 17, 18). High quality cold-pressed sunflower oil, that is most present on the market, should have distinctively pleasant and characteristic aroma, with odor and flavor of sunflower seeds (2). Unpleasant aroma of this oil is described as cardboard, grass, fat (19), sour, burned oil, roasted and burned oilseeds (3).

The investigated oil samples were described to have a „bitter“ flavor of various intensity and was characterised as mild in the oil obtained from fresh seeds to extremely unpleasant, dominant bitter flavor in oil obtained from seeds that were one year old. The main contributors to the bitter flavor, odor and aroma of the cold-pressed sunflower oils are phenolic compounds (3). One contributing factor to this unacceptable sensory finding are impurities present in the raw materials (5, 6). Rabrenović (20) also detected some bitterness in the cold-pressed pumpkin oil obtained from the older seeds. Cold-pressed sunflower oil can also have a very unpleasant, sharp flavor that causes a burning sensation and it is detected in the oils with high content of free fatty acids, usually obtained from poor quality seeds (16).

Obvious cloudy appearance, that is a quality defect compared to desirable oil clarity, is caused by many compounds, such as saturated triacylglycerols, waxes, free fatty acids, fatty alcohols, hydrocarbons, sterols and sterol esters, whose concentration is in direct correlation with the intensity of cloudness and the rate of its occurrence (21). Sunflower oil contains waxes (22), the content of which must be below 70 mg/kg in oil that is clear under the „cold“ test conditions (21). The investigated samples did not show any signs of cloudy appearance at room temperature. All samples were clear and shiny, with appealing appearance, and were not affected much by the storage time of the seeds.
Cold-pressed oils differ based on their color; however, the majority of cold-pressed oils are yellow or yellow-brownish, with red or green hues (2, 6, 23). Carotenoids (yellow pigments) present in cold-pressed oils are bioactive compounds that have antioxidative and antiradical properties and have been in focus for the last several years. Therefore, cold-pressed oils abundant in this pigment have more pronounced color, but higher nutritional value and oxidative stability (17, 20).

**Chemical quality and oxidative stability of the cold-pressed sunflower oils obtained from the seeds stored for 0, 6 and 12 months**

The chemical quality and oxidative stability parameters of the seeds stored for 0, 6 and 12 months and their respective cold-pressed oils are shown in Table 2.

Acid value is one of the basic oil quality parameters and it is in direct correlation with the presence of undesirable free fatty acids, both in seeds and cold-pressed oils. It is well known that triacylglycerols are hydrolyzed intensively during the storage time (chemical hydrolysis due to the lipase activity), which causes an increase in the seeds' and cold-pressed oil's acidity (2, 6). Published data also confirmed that sunflower seed storage time had a negative impact on the seed and oil quality due to increased contents of free fatty acids (11, 12).

Table 2. Chemical quality and oxidative stability parameters of the cold-pressed oils and seeds stored for 0, 6 and 12 months

<table>
<thead>
<tr>
<th>Parameter*</th>
<th>Storage time (months)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>0</td>
</tr>
<tr>
<td>AV (mgKOH/g)</td>
<td>0.54±0.00</td>
</tr>
<tr>
<td>- seeds**</td>
<td></td>
</tr>
<tr>
<td>- oil</td>
<td>0.49±0.01</td>
</tr>
<tr>
<td>PV (mmol/kg)</td>
<td>0.27±0.01</td>
</tr>
<tr>
<td>- seeds**</td>
<td></td>
</tr>
<tr>
<td>- oil</td>
<td>1.73±0.02</td>
</tr>
<tr>
<td>AnV (100%350 nm)</td>
<td>0.00±0.00</td>
</tr>
<tr>
<td>- seeds**</td>
<td></td>
</tr>
<tr>
<td>- oil</td>
<td>0.16±0.01</td>
</tr>
</tbody>
</table>

*Values are average of three measurements ±SD
**Determined in oils obtained using cold extraction

As expected, at the beginning of the experiment, the acid value determined in seeds was the lowest (0.54±0.00 mgKOH/g) (Table 2). Dimić et al. (7) investigated sunflower seeds stored for 3 months and reported an acid value of 1.77 mgKOH/g, which was much higher than in the fresh seeds and oils that were obtained in this study. However, the acid value in the seeds stored for 6 months was relatively high (1.29±0.01 mgKOH/g) (Table 2). The acid value in the seeds stored for one year had significantly increased and was 2.11±0.72 mgKOH/g. Hence, the highest content of the free fatty acids was determined in the oil obtained by cold-pressing of the seeds stored for 12 months, while the lowest
content was determined in the oil obtained by cold-pressing of the fresh seeds. The free fatty acid content of the analyzed oils was in the range from 0.49±0.01 to 1.95±0.02 mgKOH/g (Table 2).

The results for acid values of the cold-pressed sunflower oils obtained in this study are somewhat lower than the published ones, ranging from 0.66 mgKOH/g (24) to 3.85 mgKOH/g (4, 25). Our results are in accordance with the regulations defined by the Roolbook of quality (18) for edible unrefined oils, where the maximum for the acid value is 4.0 mg KOH/g. The low acid values for the analyzed sunflower seeds and oils showed that the raw material was of a very good quality and the seeds were adequately stored for 12 months. Đimić et al. (8) studied the impact of the storage time on the quality of the sunflower seeds and obtained oil and found an increase in the free fatty content due to the storage time. They reported the acid value of the oil extracted from the 6 month old sunflower seeds (2.07 mgKOH/g) and for the oil extracted from the 12 month old seeds (2.55 mgKOH/g). However, seeds of the oleic type variety had a lower acid value. Since oleic type sunflower seeds were naturally dried, an enzyme system was not inactivated and those seeds continued the maturing process during storage, which lowered the acid value. The same authors also concluded that with the longer seed storage time (up to 12 months), cold-pressed oils had an increased acidity. In comparison, the standard, linoleic type of sunflower seeds stored for 3 months had an acid value of 1.66 mgKOH/g, while the oil obtained from the 12-month old seeds had 2.44 mgKOH/g.

It is known that the standard type sunflower seeds are very sensitive to oxidation due to a very high linoleic fatty acid content. Therefore, it is important for the quality of the cold-pressed oils to determine their oxidative state. In order to assess the quality of the sunflower seeds and their respective cold-pressed oils, the peroxide and anisidine numbers were determined as an indication of the content of peroxides and secondary products of oxidation.

At the beginning of our experiment, the PV of the fresh seeds was only 0.27±0.01 mmol/kg, which indicated a very high quality of the raw materials. The study of the 3-month old sunflower seeds by Đimić et al. (7) indicated the PV of 0.34 mmol/kg. Based on our results (Table 2), it can be concluded that the quality of seeds decreased with storage time, where the content of primary products of oxidation, PV was 1.00±0.04 mmol/kg and 1.40±0.02 mmol/kg, after 6 and 12 months of storage, respectively.

The peroxide values of the cold-pressed oils were low, ranging from 1.73±0.02 (oil obtained from the seeds stored for 0 month) to 2.22±0.07 mmol/kg (oil obtained from the seeds stored for 12 months) (Table 2), which indicated good quality oils. These results confirmed that oxidative processes were not significantly present either in the fresh or stored seeds or during the pressing process. Our results for monitored PV are with much lower values than those published by De Leonardsis et al. (1) (4.45 mmol/kg). The cold-pressed oil content of the primary products of oxidation can be in the range of 4.45 to 6.27 mmol/kg (3), while in the cold-pressed and afterwards refined sunflower oil it was only 0.17 mmol/kg (26).

The published data also indicated that the storage time of sunflower seeds caused an increase in the content of the primary products of oxidation in the cold-pressed oil (11, 12). Đimić et al. (8) have also confirmed that the storage time of the linoleic type sunflower seeds had an impact on the increase of the primary products of oxidation. The
PV for the oils obtained from 3 and 6 months old seeds were 0.34 to 3.87 mmol/kg, respectively, while it was 6.50 mmol/kg for the oils obtained from the 12-month old seeds. The same authors concluded that the prolonged sunflower seeds (linoleic type) storage time from 3 to 12 months had the PV that increased by 4-7 times.

The results for the anisidin value (Table 2) indicate no changes for the fresh and 6-month old seeds (0.00±0.00), while the oil obtained from the 12-month old seeds had AnV of 0.86±0.53. The low AnV indicates that the investigated seeds were of good quality and did not have any significant oxidation processes detected by primary or secondary products of oxidation. The AnV of the investigated cold-pressed oils were very low, up to 0.86±0.04 (Table 2), which is much lower compared to the oils extracted by solvent, which had the AnV of 4.99 (27). Previously published data reported an AnV for the unrefined oil of 1.46 (28) and 3.72 for the refined oil (29). According to Romanić and Dimić (29), cold-pressed linoleic type sunflower oil had an AnV of 0.07, as a measure of the content of secondary oxidation products, while the oleic type had none (0.00).

Dimić et al. (8) investigated the impact of the storage time on the increased AnV in the cold-pressed sunflower oil obtained from the 12-month old seeds and reported an AnV of 1.50. The same authors obtained similar results in the cold-pressed oleic type sunflower oil, which had an AnV of 0.00-0.95 for the seeds stored for 3 months and AnV of 0.70-1.51 for the seeds stored for 12 months.

The AnV levels in the cold-pressed oil depend on the quality of the raw materials. Oomah et al. (1998) (30) reported an AnV of 3.2 for the grapeseed oil, Vujasinović (17) reported an AnV of 0.10±0.02 to 1.72±0.03 for the pumpkin seed oil, while Choo et al. (31) reported 0.36-0.74 for the flaxseed oil. Investigated extra virgin olive had AnV of 0.0 to 2-3, while virgin olive oil had 5.73 (8).

CONCLUSION

Prolonged storage time of sunflower seeds had a negative impact on the sensory quality of the cold-pressed sunflower oils, especially on flavor, odor and aroma. The seed storage time of 6 and 12 months did not have much influence on the appearance and color of the investigated oils. The analysis of the data has demonstrated that the undesirable seed changes happened during the 12-month storage time which had an impact on the sensory and chemical quality, as well as on the oxidative stability of the cold-pressed oil. Considering the data obtained in this study it could be said that the high-quality oils (according to the quality regulations) can be produced using not only fresh seeds (0 months storage time), but also 6-month old sunflower seeds. The raw materials and the seeds' storage conditions are very important parameters that have an impact on the quality of the cold-pressed oils.

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REFERENCES

18. Pravilnik o kvalitetu i drugim zahtevima za jestiva biljna ulja i masti, margarin i druge masne namaze, majonez i srodne proizvode („Službeni list SCG“, br. 23/2006 i „Službeni glasnik RS“, br. 43/2013).
УТИЦАЈ ВРЕМЕНА СКЛАДИШТЕЊА СЕМЕНА НА КВАЛИТЕТ ХЛАДНО ПРЕСОВАНОГ УЉА СУНЦОКРЕТА

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У раду је испитан утицај времена складиштења семена на квалитет хладно пресованог уља сунцокрета. Квалитет и оксидативна стабилност испитани су у уљу произведеном из свежег семена, као и из семена складиштеног 6 и 12 месеци, домаћег хибрида сунцокрета стандардног, линолног типа. Утврђено је да продужење времена чувања семена испољава неповољан утицај на све аспекте квалитета уља, нарочито на параметре сензорног квалитета тј. укус, мирис и арому. Хемијски квалитет као и оксидативна стабилност се такође нарушавају услед складиштења семена, о чему сведочи и увећање вредности киселинског и пероксидног броја уља. Киселински број уља произведеног из свежег семена имао је вредност 0,49±0,01 mgKOH/g, а уља произведеног из семена старог годину дана, 1,95±0,02 mgKOH/g. Садржај примарних продуката оксидације (пероксидни број, PV) уља, добијеног пресовањем свежег семена износио је 1,73±0,02 mmol/kg, а уља из семена складиштеног 12 месеци, 2,22±0,07 mmol/kg. У уљу произведеном из семена чувања годину дана анисидински број (AnV) је имао вредност 0,86±0,04 (100A1% 350nm).

Кључне речи: семе сунцокрета, хладно пресовано уље, време складиштења, сензорни квалитет, оксидативна стабилност

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