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The effect of roasting on the oxidation stability of vegetable oils

1. Summary

In our work, we were looking to answer the question whether the oxidation stability of apricot kernel oil and walnut oil obtained by pressing changes due to roasting. It is well known that the organoleptic properties of vegetable oils can be favorably influenced by the roasting of the seeds before pressing. Our results support the fact that the oxidation status of the oil obtained changes due to processes that take place during roasting. Our results also showed that the extent of the changes due to roasting depended very much on the starting material, in fact, in certain cases, opposite effects were observed. For example, the oxidation stability of apricot kernel oil, which is more resistant to oxidation to begin with and is rich in oleic acid, was increased by roasting, while the oxidation stability of walnut oil, rich in polyunsaturated fatty acids, was adversely affected by roasting.

As a result of the measurements it can be stated that the oxidation stability of vegetable oils is fundamentally determined by their fatty acid compositions, and roasting can increase the resistance to oxidation of those oils that are already stable to begin with.

2. Introduction

One of the important factors of vegetable oil quality is their tendency to become rancid. Resistance to oxidation is based on the combined effect of several factors. The oxidation tendency of oils is fundamentally influenced by the fatty acid composition and, in addition, the presence of substances with antioxidant effects is also important. It is so, because they can positively affect resistance to oxidation. Some of the antioxidant substances are natural components of vegetable oils, such as tocopherols, certain phenolic compounds, including oleuropein, hydroxytyrosol in olive oil, gamma-oryzanol in rice bran oil and sesamin in sesame oil. In addition, antioxidant compounds can also form during processing, for example, due to the preliminary roasting of oilseeds.

It was determined by Durmaz and his research group **[1]** that the extraction yield of naturally occurring antioxidants is generally improved by roasting processes, and according to Mohos **[2]**, roasting is a heat transfer process, during which plant seeds are heated, with agitation, to temperatures over 100 °C. The purpose of roasting, on the one hand, is to improve the organoleptic properties of the seeds by producing flavor and aroma substances, and also to remove the possibly present volatile acids with unpleasant sensory effects.

In addition, by reducing the water content, further processing and pressing of the oil is facilitated by roasting. The effectiveness of the operation is influenced by several factors, so roasting is affected by the size and uniformity of the seeds, as well as the efficiency of chopping. Durmaz and Gökmen **[3]** reached a conclusion that the antioxidant effect and the oxidative stability of roasted seeds is higher than those of unroasted seeds. Roasting improves digestibility and organoleptic properties, provides microbiological safety, extends shelf-life, enhances flavor, color and texture, inactivates enzymes, thus increases oil yields. Oxidation stability in the oil is increased by the inactivation of the enzymes. However, it has to be stated that the roasting of oilseeds has an optimum. Jannat et al. **[4]** showed that roasting at a temperature of 220 °C or higher results in a significant decrease in the amount of antioxidant substances (especially polyphenols).

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3. Materials and methods

3.1. Materials used and sample preparation

Cleaned apricot and walnut kernels were used for our experiments, both of which were purchased directly from the producer. Kernels were roasted using an I-Roast homemade roasting equipment. The temperature treatment program that did not yet cause charring or unfavorable change in the organoleptic properties of the seeds was determined during preliminary experiments. The latter could be determined simply and unequivocally by visual inspection and tasting. Accordingly, roasting of apricot kernels was performed at a temperature of 160 °C for 3 minutes, while walnut kernels were roasted at a temperature of 160 °C for1 minute. In both cases, treatment was concluded by a 4-minute cooling phase. Following this, oil from the seeds was hand-pressed (Piteba oil expeller, distributor: Kétezeregy Bt., Budakalász). Pressing temperature was 50 °C, the oil obtained was allowed to settle at room temperature for 48 hours and the clarified oil was then decanted. Oil samples were stored in the dark at room temperature in PET preforms until the analyses.

3.2. Analytical methods

In order to characterize the oils included in the experiment, their fatty acid contents were measured. Analyses were carried out by a gas chromatographic method, with methyl esterification based on standards ISO 5508:1990 and ISO 5509:1990. Measurements were performed only on the unroasted oils, because short-term thermal treatment at 160 °C does not affect fatty acids **[5].**

To assess the effects of roasting, the acid number, peroxide value, anisidine value, UV absorbance at 232 and 268 nm, color change, oxidation stability and organoleptic properties of the samples were determined.

Acid number was determined according to MSZ ISO 660:2008 **[8]**, while peroxide value according to MSZ 19823:81 **[9]**, performing three parallel measurements in each case.

The so-called secondary oxidation products formed during the oxidation processes of vegetable oils are mainly aldehydes, the amount of which is indicated by the anisidine value. This is determined spectrophotometrically. Measurements were carried out according to MSZ ISO 6885:1992 **[10]**.

Characteristic compounds of the oxidation-rancidification processes of lipids are conjugated dienes and trienes, and on the basis of their measurement one can draw conclusions regarding the extent of oxidation. The amounts of these compounds can be determined spectrophotometrically at 232 nm and 268 nm. Their measurement was performed according to MSZ ISO 3656:1990 **[11]** and Annex IX of the Hungarian Food Codex 3-1-2568/91. **[12]**.

Oxidation stability of the samples was measured using a Rancimat 743 (Metrohm) instrument. Air is passed through the heated sample by the instrument, and the volatile compounds produced are absorbed in distilled water. By continuously measuring the changing conductivity of the water, the moment can be determined when the second derivative of the function describing the conductivity as a function of time reaches a maximum. This point is called the induction time, and it is considered to be one of the indicators of the oxidation stability of oils **[13]**. In our experiments, measurements were carried out at a temperature of 110 °C and an air flow rate of 20 l/h.

The extent of the color change due to roasting was determined by a Minolta C-300 instrument in the L* a* b* tristimulus system.

To determine the aroma-forming effect of roasting, a sensory testing was organized. Unroasted and roasted oil samples were evaluated by a panel consisting of 30 laypeople. Samples were evaluated by the testers along six different aspects, by positioning the samples on an unstructured scale between the two extreme values (the complete absence of the property and the theoretical maximum). The aspects: the depth of yellow color, odor intensity, the intensity of roasted flavor, the intensity of bitter taste, the intensity of rancid taste and the degree of preference. The distance of the points characterizing the samples from the end-point indicating the absence of the aspect were expressed as the percentage of the total scale and this was considered to be the measurement result. Average values of the results were calculated and the sensory profiles of the samples thus obtained were depicted on radar diagrams.

4. Results and evaluation

Fatty acid composition results of cold pressed oils are summarized in **Table 1**.

Data in **Table 1** show that our results are consistent with literature reports **[2]**. The valuable component of walnut oil is alpha-linolenic acid (18:3), which was present in the sample in an amount of 6.2%, while apricot kernel oil was characterized by a high oleic acid (18:1) content. The total saturated fatty acid content of walnut oil was 12.6%, while in the case of apricot kernel oil it was only 8.1%. The amount monounsaturated fatty acids was 29% in walnut oil and 60.5% in apricot kernel oil. The amounts of polyunsaturated fatty acids were 57.7% and 30.7%, respectively. According to our results, the most pronounced differences between the two oils were in the amounts of monounsaturated and polyunsaturated fatty acids.

The oxidation stability of vegetable oils is also related to the amount of free fatty acids, which is indicated by the acid number. Acid numbers of the oils obtained from unroasted and roasted kernels are shown in **Figure 1**.

According to the requirements of the Hungarian Food Codex, the acid number of cold pressed and virgin oils cannot exceed 4, this was satisfied by all samples, although the acid number of the unroasted walnut oil was just at the limit value. On the other hand, the acid number of 2.5 of the unroasted apricot kernel oil can be considered moderate. In the case of both oils, it could be observed that the acid number values decreased due to roasting. The extent of this was more pronounced in the case of apricot kernel oil, since its acid number value changed from 2.67 to 1.01.

Oxidation processes of vegetable oils can be partially characterized by the peroxide value. Peroxide values of the oils tested are shown in **Figure 2**.

According to our measurement results shown in **Figure 2**, peroxide values satisfy food codex requirements (the maximum value for the product group is 10). Of unroasted oils, walnut oil presented the higher value. It can be observed that peroxide values, indicating the intensity of primary oxidation processes, increased due to roasting, although they did not exceed the limit value. In absolute terms, the increase was larger in the case of walnut oil. This result is consistent with the communication of Martinez et al., according to which the primary oxidation processes of walnut oil show an exponential growth **[6]**.

Anisidine values characteristic of secondary oxidation processes are shown in **Figure 3**.

There is no limit value for the anisidine value of vegetable oils in the Hungarian Food Codex, but it can be generally stated that anisidine values above 20 indicate significant oxidation. Anisidine values shown in **Figure 3** are considered low (4.41 for unroasted walnut oil, 0.12 for unroasted apricot kernel oil). Anisidine values increased in both oils due to roasting. In absolute terms, the increase was larger in the case of walnut oil, but it was still not extremely large.

During the oxidation of polyunsaturated fatty acids due to heat treatment, for some of the double bonds the sequence with interrupting methylene groups is replaced by the conjugated position, therefore, the amount of conjugated fatty acids is an indicator of thermal oxidation.

UV absorbance is characteristic of polyunsaturated conjugated compounds. Results obtained during UV absorbance measurements are shown in **Table 2**.

From the results summarized in **Table 2** it was determined that UV absorbances increased at both wavelengths for both oils due to roasting. This phenomenon indicates that, due to thermal stress, positional isomerization also occurred in the samples. The increase was smaller in the case of apricot kernel oil, while it was more pronounced for walnut oil. The absorbance at 268 nm, indicating the amount of conjugated trienes, was significantly higher for walnut oil than it was for apricot kernel oil.

Oxidation stabilities of the samples, measured by a Rancimat instrument and expressed as induction times are shown in in **Figure 4**.

Results in **Figure 4** show that the induction time characterizing the oxidation stability of apricot kernel oils exceeded significantly the value measured for walnut oil, both in the case of unroasted and roasted kernels. As a result of roasting, the induction time decreased for walnut oil, while it increased for apricot kernel oil. This result indicates that, while apricot kernel oil became more resistant to oxidation as a result of roasting, the opposite was true for walnut oil. Similar results have been reported by Jau-Tien Lin et al. **[5]** when examining the rancidification tendency of apricot kernel due to roasting. Color characteristics measured in the CieLab system are shown in **Table 3**.

Results presented in **Table 3** indicate that the color characteristics of the samples changed similarly due to roasting. Lightness (L) values decreased due to roasting, i.e., the color of the samples deepened. The a* value indicating the green-red transition increased, indicating the development of a reddish character. The b* value characteristic of the blue-yellow transition decreased as a result of roasting for both oils, so the yellowish color decreased in the samples. Combined analysis of the three color indicators showed that the color of the samples deepened as a result of roasting, which can be assumed to indicate a transformation of yellowish color components into ones with reddish characteristics.

One of the goals of roasting is to improve the aroma characteristics of the oils, and this effect was analyzed during sensory testing. Aroma profiles of the samples tested are shown in **Figure 5**.

Based on the aroma profile (**Figure 5**) it can be stated that there have been significant changes in the organoleptic properties of both oils due to roasting. Oils prepared from roasted kernels were characterized by a more intense yellow color, an increased odor intensity, the dominance of the roasted flavor, a somewhat increased bitter taste and, in general, an increased preference. There was no significant difference between the two kinds of oil, although in the case of the walnut oil the roasted flavor character and the bitter taste was more intense than in the case of the apricot kernel oil. However, this was accompanied by an increase in general preference, indicating that the roasted flavor and the bitter taste had a rather positive effect.

5. Conclusions

Results demonstrated that a relatively mild roasting (160 °C, roasting times of 1 or 3 minutes) can have a significant effect on the oxidation stability and organoleptic properties of oils. The roasting used in the experiment had a clearly positive impact on organoleptic properties of and the preference for the kernel oils tested, confirming that it is justified to use roasting before pressing in the production of vegetable oils.

In the cases of the acid number, the peroxide value, the anisidine value, the UV absorbance and the color characteristics, the direction of the change was the same for both oils, however, in the case of the oxidation stability measured using the Rancimat method, the directions of the change were opposite. For unroasted oils, the acid number, peroxide value and anisidine value of apricot kernel oil were lower than those of walnut oil. It can be concluded from this fact that, of the two oils, apricot kernel oil is more stable to begin with, it is more resistant to oxidation. This is primarily related to the fatty acid composition. The oxidation rate of monounsaturated fatty acids is one tenth of that of doubly unsaturated ones and only one twenty-fifth of that of triply unsaturated ones **[7].** According to our results, this stability is strongly related to the extent of fatty acid unsaturation. Taking into consideration that the Rancimat test is related to the kinetics of the formation of volatile components, we concluded that volatile compounds are formed by the cleavage of unsaturated bonds, so this process is more pronounced in the case of polyunsaturated compounds. It can be concluded from the decrease in the acid number for both oils that the processes initiated by the thermal treatment used in the experiment are accompanied by the transformation of free fatty acids. This fact is considered to be favorable from an oil quality point of view.

6. References

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