RESEARCH ON THE MODIFICATION OF PHYSICOCHEMICAL VALUES OF WALNUT FRUITS FROM HARVEST (GREEN) TO STORAGE (DRY)

CERCETĂRI PRIVIND MODIFICAREA VALORILOR FIZICO-CHIMICE A FRUCTELOR DE NUC DE LA RECOLTARE (ÎN VERDE) PÂNĂ LA PĂSTRARE (ÎN USCAT)

GHERGHEL Madalina-Iuliana[1], TURCU Cristina-Ionela[1*], BUȚERCHI Ioana[2], ISTRATE Mihai[2], CORNEANU Margareta[1], IUREA Elena[1]

*Corresponding author e-mail: ingcristinaboboc@gmail.com

Abstract.

This paper analyzes the physicochemical characteristics of fruits from the moment of harvest to their storage under controlled conditions. The study focuses on the changes occurring in the composition and quality of fruits during various stages of post-harvest. The analysis includes parameters such as soluble solids, acidity index, titratable acidity, and moisture content, and explores how these parameters evolve throughout the post-harvest process. Observations indicate an increase in the value of soluble solids during the storage (drying) of walnut kernels. Regarding total acidity content, it is higher at harvest and decreases during fruit dehydration. However, some varieties exhibited an increasing trend in acidity, with higher levels of organic acids during storage, due to natural drying of the kernel. Varieties with a high acidity index showed greater concentrations of oleic acids or they may have higher levels of rancidity. This paper contributes to a better understanding of the physicochemical changes in fruits post-harvest and provides recommendations for optimizing handling and preservation processes, aimed at maintaining fruit quality and nutritional value over time.

Key words: walnuts, fruit quality, preservation.

Rezumat.

Lucrarea de față analizează caracteristicile fizico-chimice ale fructelor de la momentul recoltării până la păstrarea acestora în condiții controlate. Studiul se concentrează pe modificările care apar în compoziția și calitatea fructelor în diverse etape ale post-recoltării. Analiza include parametri precum substanța uscată solubilă, indicele de aciditate, aciditatea titrabilă și conținutul de umiditate și explorează modul în care acești parametri se modifică pe parcursul procesului de post-recoltare. Observațiile efectuate indică o creștere a valorii substanței uscate solubile pe parcursul păstrării (uscării) miezului de nucă. În ceea ce privește conținutul acidității totale, acesta este mai ridicat la recoltare și scade pe parcursul deshidratării

[1] Research Station for Fruit Growing Iasi, Romania

[2] "Ion Ionescu de la Brad" Iasi University of Life Sciences, Romania

fructelor. Totuși, unele soiuri au avut o evoluție crescândă a acidității, cu un conținut mai ridicat în acizi organici pe parcursul păstrării, datorită uscării pe cale naturală a miezului. Soiurile cu indicele de aciditate ridicat, prezintă o concentrație mai mare în acizi oleici și se poate spune că acestea au cel mai mare conținut în acizi oleici, ori au un grad de râncezire mai accentuat. Lucrarea contribuie la o mai bună înțelegere a modificărilor fizico-chimice ale fructelor post-recoltare și oferă recomandări pentru optimizarea proceselor de manipulare și conservare, în scopul menținerii calității și valorii nutritive a fructelor pe termen lung.
Cuvinte cheie: nuci, calitatea fructelor, păstrare.

INTRODUCTION

Research on the post-harvest quality of horticultural crops has emphasized the importance of monitoring chemical changes, such as acidity, soluble solids, and lipid stability, to maintain freshness and nutritional value [Kader, 2013]. Studies on nuts and fruits, like walnuts and pistachios, highlight that lipid degradation and changes in acidity levels are indicators of quality loss over time, influenced by storage conditions [Patraș and Dorobanțu, 2010; Ozkan and Koyuncu, 2005]. In walnuts, for instance, high lipid content (up to 70%) and its tendency to oxidize affect both shelf life and flavor, making parameters like the acidity index critical for evaluating post-harvest quality [Ozkan and Koyuncu, 2005].

Similarly, acidity levels, including titratable acidity and malic acid content, are essential for determining flavor profiles and consumer preference, as these attributes impact both taste and perceived freshness [Patraș and Dorobanțu, 2010]. Changes in acidity can signal ripening or spoilage, which is particularly important in storage and transport settings where temperature and humidity fluctuations may accelerate these transformations [Kader, 2013]. This literature underlines the need for multi-parameter analysis to optimize storage practices, aiming to extend the shelf life of high-quality produce while preserving its sensory and nutritional properties.

MATERIAL AND METHOD

The material consisted of 10 native and foreign walnut varieties, cultivated in the Northeast region of Romania at the Iasi Research and Development Station for Fruit Growing. Samples were collected at consumer maturity; some were prepared for analysis at harvest, in their fresh state, while others were stored for later analysis in a dry state.

Various physicochemical indicators were analyzed, including: soluble dry substance (SUS%), acidity index (IA), titratable acidity (AT), and moisture content in the walnut kernels.

Soluble Dry Substance (SUS) - For solid products lacking natural juice, the soluble dry substance is measured by extracting water-soluble compounds (such as sugars and acids) from a finely ground sample. Distilled water is added to the ground sample, allowing these soluble compounds to dissolve. The mixture is then filtered to obtain a clear solution.

This solution is analyzed using a refractometer, which measures the refractive index based on the concentration of dissolved solids. The SUS value is read in degrees

Brix, reflecting the percentage of soluble substances (SUS) in the original product. [STAS 145/20-88, 1988].

Acidity Index (IA) - measures the content of free fatty acids in the oil extracted from the walnut kernel, reflecting the degree of lipid degradation. Acidity is determined by titrating the oil with a standard solution of potassium hydroxide (KOH) or sodium hydroxide (NaOH) in the presence of an indicator (phenolphthalein) [Maskan and Karatas, 1998]. The oil obtained from the kernel is dissolved in an alcohol-ether mixture and titrated with the hydroxide solution until the indicator's endpoint. The result expresses the amount of KOH needed to neutralize the free fatty acids, relative to the sample's weight [Savage *et al.,* 2001].

Titratable Acidity (AT) - measures the total amount of organic acids present in the walnut kernel. This is determined by titrating a sample suspension with an alkaline solution (typically NaOH) to a specific pH, using a pH indicator. The ground sample is mixed with distilled water, and the resulting solution is titrated with NaOH to pH 8.1 (or until the indicator shows the specified color), expressing acidity in acid equivalents per 100 g of product [Anonymous 1990 and 1991].

Moisture content - determined by the gravimetric method, where the kernel sample is heated in a dryer at a specific temperature to evaporate the free water. The weight loss of the sample is used to calculate moisture content. A precise amount of kernel is weighed, dried at 103°C (or according to the applicable standard method) until constant weight, and the weight loss is considered the water content in the sample, expressed as a percentage [Anonymous 1990 and 1991].

These methods allow for evaluating the quality of the walnut kernel, providing information on its storage stability and preservation potential.

RESULTS AND DISCUSSIONS

Soluble Dry Substance (SUS) represents soluble compounds (sugars, acids) and serves as an indicator of maturity and flavor concentration. In January, most varieties showed an increase in SUS, suggesting a higher concentration of soluble compounds due to water loss during storage. Varieties with significant increases include Miroslava (from 10.5 to 13.97), Ovidiu (from 7 to 10.87), and Sibișel (from 10 to 11.73), indicating a sweeter and more concentrated flavor profile after storage.

Table 1

Soluble Dry Substance (SUS) from harvest to dry

Varieties	SUS % at Harvest	SUS % Dry
Anica	**6^{g}**	**9.90^{d}**
Bortko	**6.2^{g}**	**8.97^{f}**
Danirenko	**9.7^{b}**	**9.53^{d}**
Germisara	**8.2^{c}**	**9.52^{d}**
Jupânești	**7^{e}**	**10.07^{c}**
Miroslava	**10.5^{a}**	**13.97^{a}**
Ovidiu	**7^{e}**	**10.87^{c}**
Prezident	**7.8^{d}**	**10.47^{c}**
Sibișel	**10^{a}**	**11.73^{b}**
Velnița	**6.7^{f}**	**10.23^{c}**

Titratable acidity reflects the total level of organic acids. Changes between November and January vary across varieties.

Significant increases in AT were observed in varieties such as Anica (from 3.58 to 3.81) and Prezident (from 3.55 to 4.74), suggesting an intensification of acidic characteristics.

Notable decreases were recorded in varieties like Bortko (from 3.94 to 1.82) and Danirenko (from 3.17 to 2.02), which may indicate a reduction in acidity, possibly associated with a loss of freshness.

Varieties with high SUS values tend to have stable or slightly increased titratable acidity, indicating a balance in flavor between sweetness and acidity.

Table 2

Titratable Acidity (AT) from harvest to dry

Varieties	AT (meq/100 g prod) at Harvest	AT (meq/100 g prod) Dry
Anica	**3.58^{a}**	**3.81^{b}**
Bortko	**3.94^{a}**	**1.82^{f}**
Danirenko	**3.17^{a}**	**2.02^{e}**
Germisara	**3.14^{a}**	**2.75^{c}**
Jupânești	**3.17^{a}**	**3.04^{b}**
Miroslava	**3.17^{a}**	**3.30^{b}**
Ovidiu	**2.91^{a}**	**2.24^{d}**
Prezident	**3.55^{a}**	**4.74^{a}**
Sibișel	**3.87^{a}**	**3.10^{c}**
Velnița	**2.59^{b}**	**3.58^{b}**

Malic acid contributes to the perception of acidity and the overall taste of the product. Varieties like Prezident (from 0.24 to 0.32) and Velnița (from 0.17 to 0.24) show an increase, suggesting an intensification of acidic flavor during storage. Bortko and Danirenko recorded decreases (e.g.: from 0.26 to 0.12 for Bortko), indicating a reduction in freshness or a shift in the acidic profile.

Varieties with high AT values tend to exhibit stable or slightly increased malic acid levels, suggesting a more balanced flavor profile and a potential improvement in acidity perception.

Table 3

Malic Acid from harvest to dry

Varieties	AT (ac. malic/100 g prod) at Harvest	AT (ac. malic/100 g prod) Dry
Anica	**0.24^{a}**	**0.26^{b}**
Bortko	**0.26^{a}**	**0.12^{g}**
Danirenko	**0.21^{b}**	**0.14^{f}**
Germisara	**0.21^{b}**	**0.18^{d}**
Jupânești	**0.21^{b}**	**0.20^{c}**
Miroslava	**0.21^{b}**	**0.22^{b}**
Ovidiu	**0.20^{c}**	**0.15^{f}**
Prezident	**0.24^{a}**	**0.32^{a}**
Sibișel	**0.26^{a}**	**0.21^{e}**
Velnița	**0.17^{d}**	**0.24^{b}**

The acidity index (IA) reflects the level of free fatty acids and, thus, the degree of lipid oxidation, which impacts freshness and stability. Varieties like Danirenko (from 0.73 to 1.77) and Jupânești (from 1.06 to 1.42) showed substantial lipid degradation during storage. Varieties such as Prezident and Sibișel also experienced moderate increases, indicating stable quality over the medium term.

An increase in IA is inversely correlated with SUS, particularly in varieties like Bortko, where a decrease in soluble acids (AT and malic acid) corresponds to accelerated lipid degradation.

Table 4

Acidity Index (IA) from harvest to dry

Varieties	IA (mg KOH/1g prod) at Harvest	IA (mg KOH/1g prod) Dry
Anica	**0.63^{c}**	**1.21^{b}**
Bortko	**0.95^{b}**	**1.03^{c}**
Danirenko	**0.73^{b}**	**1.77^{a}**
Germisara	**1.10^{a}**	**0.91^{d}**
Jupânești	**1.06^{a}**	**1.42^{b}**
Miroslava	**0.84^{c}**	**1.16^{b}**
Ovidiu	**1.08^{a}**	**1.08^{b}**
Prezident	**0.77^{b}**	**1.33^{b}**
Sibișel	**0.90^{b}**	**1.25^{b}**
Velnița	**0.50^{d}**	**1.01^{c}**

Significant differences between varieties indicate that certain cultivars possess distinct chemical characteristics that can influence product quality and stability during storage.

Storage significantly impacted the analyzed parameters, with noticeable changes in the ranking of varieties between harvesting and storage.

Varieties with high stability, such as Miroslava and Sibișel, maintained elevated SUS and acidity levels, making them suitable for long-term storage.

Varieties with significant variations, such as Bortko and Danirenko, exhibited notable decreases or increases in specific parameters, suggesting greater sensitivity to storage conditions.

CONCLUSIONS

Most varieties showed an increase in SUS from harvesting to dry, indicating a natural maturation process and sugar concentration. Varieties like **Miroslava** and **Sibișel** maintained high SUS values, suggesting superior sweetness and quality, which correlates with the improved taste over time.

Acidity levels generally increased, especially in varieties like **Prezident** and **Velnița**, showing stronger acidic profiles. This suggests a balance between sweetness (indicated by SUS) and acidity, which may improve the flavor complexity of these varieties during storage.

Prezident and **Velnița** showing significant increases in malic acid content. These changes reinforce the trends seen in the titrable acidity table, where rising

acidity levels align with the increase in malic acid, enhancing the perceived tartness of these varieties.

Varieties such as **Danirenko** and **Prezident** showed substantial increases in the acidity index, suggesting lipid degradation and the release of free fatty acids, which can affect overall quality. This increase in the acidity index correlates negatively with the product's freshness, possibly reducing the shelf life of these varieties.

In summary, the data indicates that while sweetness and acidity balance improve in certain varieties, lipid degradation (as shown by the acidity index) could negatively impact the overall quality and storage potential of some products.

General conclusions

Variations in acidity and chemical composition:

The data shows significant changes in terms of acidity and the acidity index for some varieties between harvest to storage. Varieties with large increases in acidity or in the acidity index may indicate a deterioration in product quality or faster ripening.

Stability of certain varieties:

Varieties like Miroslava and Prezident showed stable increases in their characteristics, which may suggest superior quality and good adaptability in storage conditions.

Decreases in acidity:

In some varieties, such as Bortko and Ovidiu, the decreases in acidity may be a sign of freshness loss or biochemical transformations that have reduced the initial product quality.

This interpretation suggests that it is important to monitor these variations in order to adjust storage conditions and determine which varieties are the most stable and offer consistent quality over the long term.

ACKNOWLEGMENTS

This work was funded under the THEMATIC PLAN regarding the Implementation of the "ASAS Strategy for Research – Development – Innovation in Pomology" for the period 2021–2027 by ICDP Pitești – Mărăcineni and the network of Fruit-Growing Stations.

REFERENCES

1. *****, 1990 and 1991** - *Turkish standard institute: physical and chemical standards for walnut quality.* Turkish Standards Institute, Ankara, Turkey.
2. **Kader A.A., 2010** - *Postharvest technology of horticultural crops - An overview from farm to fork.* Ethiop .J. Appl. Sci. Technol, special issue no.1, p. 1-8.
3. **Maskan M. and Karatas S., 1998** - *Fatty acid composition and quality characteristics of some turkish pistachio varieties.* European Journal of Lipid Science and Technology, vol. 100, no. 7, p. 280-284.
4. **Ozkan G. and Koyuncu M.A., 2005** - *Physical and Chemical composition of some walnut (Juglans regia L.) genotypes grown in Turkey.* Grasas y Aceites, vol. 56, no. 2, p. 141-146.
5. **Patraș A. and Dorobanțu P., 2010** - *Physical and chemical composition of some walnut (Juglans regia L) biotypes from Moldavia.* Lucrări Științifice, Seria Agronomie, vol. 53, no. 2.
6. **Savage G.P., McNeil D.L., Dutta P.C., 2001** - *The nutritional composition of walnuts (Juglans regia L.).* Food Reviews International, vol. 17, no. 4, p. 319-335.
7. **STAS 145/20-88, 1988** - *Determination of moisture content in oilseeds.*