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APPLICATION OF APPLE ACIDIFIER IN VEGETABLE STEW OF TYPE „ZACUSCA” PRODUCTION

Diana Cruciurescu^{1,2}, ORCID: 0000-0002-6612-9937

¹Scientific-Practical Institute of Horticulture and Food Technologies,
59, Vieru str., Codru, Chisinau, Republic of Moldova

² Technical University of Moldova, 168, Stefan cel Mare Blvd., Chisinau, Republic of Moldova

*Corresponding author: Diana Cruciurescu: diana.cruciurescu@saiem.utm.md

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Abstract: The insufficiency of natural acidifiers in the food industry is a major problem today. The present study analyzes the acidifier from the unripe apples of variety *Golden Rezistent*. It had a significant amount of acidity (1.97 %) and impressive of total soluble substances (8.47 %). Malic acid and fructose were predominant with values of 32.95 g/dm³ and 45.55 g/dm³, respectively. The glucose content was 2 times lower than that of fructose, but citric acid and sucrose had very low concentrations. The acidifier was applied to the preparation of vegetable stew of type "Zacusca" under laboratory conditions. The recipe and the production technological scheme were developed. Physicochemical and sensorial indices were determined in the experimental samples. The elaborated product presented very good results compared to other similar foods, being appreciated with the maximum score. The implementation of the natural acidifier, obtained from thinned unripe apples in the food industry, is a key factor for the development of new healthy and ecological foods with a high nutritional value.

Keywords: *apple acidifier, sensory evaluation, physicochemical parameters, unripe apples,*

vegetable stew of type „Zacusca”.

Rezumat: Insuficiența acidifiantilor naturali în industria alimentară este o problema majoră în prezent. Studiul de față analizează acidifiantul din merele necoapte soi *Golden Rezistent*. Acesta a avut o cantitate semnificativă de aciditate (1,97 %) și impunătoare de substanțe solubile totale (8,47 %). Acidul malic și fructoza au fost predominante cu valorile de 32,95 g·dm⁻³ și, respectiv, 45,55 g·dm⁻³. Conținutul de glucoză a fost de 2 ori mai mic față de cel ai fructozei, iar acidul citric și zaharoza au avut concentrații foarte mici. Acidifiantul a fost aplicat la prepararea tocanei de legume tip „Zacusca” în condiții de laborator. Au fost elaborate rețeta și schema tehnologică de producere. În mostrele experimentale au fost determinați indicii fizico-chimici și senzoriali. Produsul elaborat a prezentat rezultate foarte bune în comparație cu alte alimente similare, fiind apreciate cu punctaj maxim. Implementarea acidifiantului natural, obținut din merele necoapte rărite în industria alimentară, reprezintă factor cheie pentru dezvoltarea alimentelor noi sănătoase și ecologice cu o valoare nutritivă înaltă.

Cuvintele-cheie: *acidifiant din mere, evaluare organoleptică, indicii fizico-chimici, mere imature, tocană de legume tip „Zacusca”.*

Abbreviations: CE – capillary electrophoresis; DAFB – days after the full bloom; GD – Government Decision; HPLC – high-performance liquid chromatography; TA – titratable acidity, expressed in malic acid; TSS – total soluble solids; TS – total sugar.

1. Introduction

The insufficiency of natural sources of acidity in the food industry is a major problem today. Long-term consumption of food products containing synthetic additives affects the consumer's health, causing disturbances in the immune system. The health of the population and the consumption of ecological and beneficial foods for the human body required researchers to find alternatives to the chemical acids used for their production.

Apple acidifier represents the unfermented juice produced from unripe apples, obtained as a result of thinning or physiological fruit drop. Recent research has shown that it is a good source of natural acidity, containing and other valuable nutrients, and it is of major interest in the food industry [1, 2]. At the lab-scale, experimental samples of acidifier were obtained from unripe apples. It was then successfully applied to the production of marinated tomatoes and canned cucumbers as an alternative to acetic acid, similar to the application of verjuice [3-5].

Vegetable stew "Zacusca" is very popular among consumers in the Republic of Moldova. It is a dish of vegetables cooked on fire or fried in oil, found in several countries of the Balkans. The main ingredients are grilled eggplant and red bell peppers, and chopped onions. Other vegetables can also be added to the stew [6].

There are several varieties of this vegetable stew, but eggplant zacusca is the most widespread and one of the most liked. Being consistent, fine and with a very pleasant aroma of grilled vegetables, this type of stew is consumed, most of the time, as an appetizer. In addition to this fact, this type of zacusca, produced over an open fire (grilled), is not standardized and has no normative documents according to which it could have been a factory on an industrial scale. All the information about the recipes are collected from people or from the internet.

Classic eggplant zacusca is made from eggplant (min. 60 %), bell peppers red (min. 40 %), onion (min. 10 %), sunflower oil (4.264 %), broth or tomato juice (4.7 %), salt (1 %), spices (pepper – 0.036 %) [7]. Also, some manufacturers add sugar, to increase the sweet taste of the product, and acetic acid, to increase the acidity, fixation and accentuation the taste and the aroma of the vegetables.

Currently, consumers choose food products that contain as few calories as possible and with natural ingredients in its composition. Thus, it was proposed to produce, under laboratory conditions, the vegetable stew identical to the classic zacusca with some changes compared to the traditional recipe. Apple acidifier was included as a source of acidity. This was obtained without the use of oil, of fried onions, sugar and acetic acid, with the aim of obtaining a dietary product, which will allow consumption by people with problems of gallbladder and liver [8]. At the same time, the exclusion of oil will favor increasing the shelf life of the product.

At the same time, the preparation of vegetable stew of type "Zacusca" will allow the widening of the assortment of such products and will make possible the implementation of the apple acidifier in the healthy foods production.

The aim of this work was to obtain experimental samples of vegetable stew type "Zacusca" with the application of apple acidifier and to evaluate the quality indices of the elaborated products.

2. Materials and methods

2.1 Raw materials and materials

Raw materials for prepare of apple acidifier served unripe apples, in the early ripening phase, of the variety *Golden Rezistent* (Figure 1). The fruits were picked in June 26, 2019 (which presented the 71st DAFB) from the experimental lots of the Scientific-Practical Institute of Horticulture and Food Technologies, Chisinau, Republic of Moldova. Physico-chemical indices of the harvested fruits were determined and presented by Crucirescu in her work [2].

Golden Rezistent is a variety obtained in SUA. It is considered a kind of perspective. The trees are demanding to the soil, have high winter hardiness and secetă. It has stable scab resistance and high resistance to powdery mildew. The fruit is of medium to large size with a mass of 150-160 g, it has a conical-oblong to conical-truncated shape and a smooth surface. Colour of apple is yellow and of pulp is white-cremy. It bears fruit in abundance early and the flowering season is medium. Requires the thinning. The variety is authorized for all areas of the Republic of Moldova [9].



Figure 1. Image of apple fruits of the *Golden Rezistent* variety [9].

For the production of vegetable stew of type "Zacusca" the following vegetables were used as raw material: eggplants (*Solanum melongena* L.), red bell peppers (*Capsicum annum* L., *Grossum Bell* group) and tomatoes (*Solanum Lycopersicum* L.) procured by on the local market. These corresponded to the normative documentation in force GD no. 929, 2009 [10]. At the same time, such secondary and auxiliary materials as table salt (GD no. 596, 2011) [11], apple acidifier, glass jars with a volume of 0.42 dm³ and Twist-off lids were used.

2.2 Location of research

Obtaining the experimental samples and determining the quality indices in the developed products were carried out within the Food Technologies department, the Food Products Quality Verification laboratory, Scientific-Practical Institute of Horticulture and Food Technologies, Chisinau, Republic of Moldova.

2.3 Technology of Apple Acidifier Production

Obtaining the acidifier from unripe apples of the *Golden Rezistent* variety harvested around the 71st DAFB was carried out according to patent no. 1286 BOPI and similar to the technological production scheme described by Crucirescu in her work [5, 12].

2.4 Technology of Vegetable Stew of type „Zacusca” Production

The experimental samples of vegetable stew of type "Zacusca" were prepared in laboratory conditions according to the production recipe shown in Table 1.

Table 1

Recipes for making vegetable stew of type „Zacusca” [13]

Raw materials and materials	Manufacturing recipe for 1000 g finished product, g
Eggplants	640
Bell peppers red	400
Tomatoes	118
Salt	10
Apple acidifier	30

Laboratory-scale processing to obtain of vegetable stew of type „Zacusca” is presented in the Figure 2.

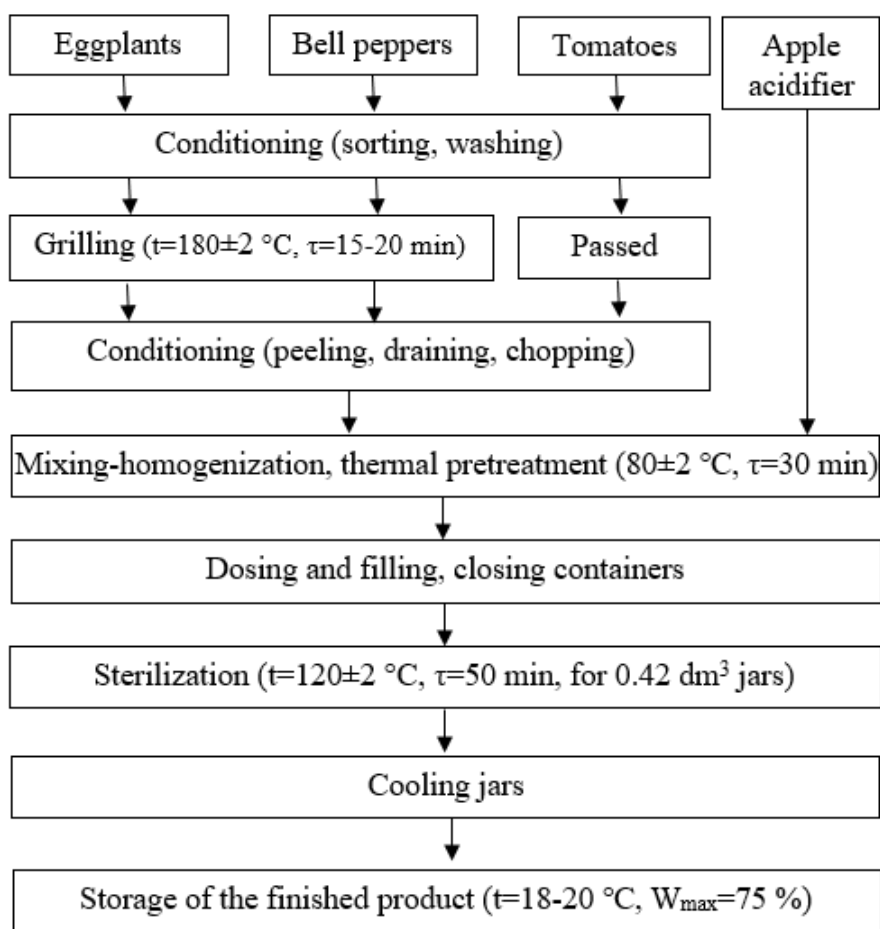


Figure 2. Lab-scale processing of vegetable stew of type „Zacusca”.

The raw material for the production of vegetable stew of type "Zacusca" (eggplants, bell peppers and tomatoes) was received, sorted and washed. Eggplants and bell peppers

were baked on an open fire (grilled) at a temperature of about 180 ± 2 °C for 15-20 min. Then they were well cleaned of the skin, but bell peppers and seeds, and left to drain the liquid in a cool place for 3-4 hours. During this time, the tomatoes were washed, passed through graters (passed) with the separation of the skin and placed on the fire in a cast iron pot. After the eggplants and bell peppers drained of their own juice, they were cut into small cubes and included in the bowl with the tomatoes, where they were homogenized and left to boil for 30 min. Periodically the whole mass was mixed. Towards the end, the apple acidifier and salt were added to the vegetable dish. After the passage of time, in jars of 0.42 dm^3 washed and conditioned, the vegetable stew was dosed with a temperature of no less than 80 ± 1 °C, closed with Twist-off lids and sterilized at a temperature of 120 ± 2 °C for 50 min, followed by cooling and labeling. The storage and preservation of the cans obtained from the "Zacusca" type vegetable stew took place at a temperature of 19 ± 1 °C and a maximum relative humidity of 75 % for 9 months.

2.5 Physical and Chemical Analysis

2.5.1 Analyzes in the acidifier in apples

Preparation of apple acidifier samples for analysis, determination of total soluble solids (TSS) (using the electronic refractometer ATAGO PAL-3), titratable acidity (TA) (ISO 750:1998) and ionic acidity (pH) (ISO 1842:1991), as well as the determination of the content of organic acids by the HPLC technique and of carbohydrates by the capillary electrophoresis (CE) method were carried out according to the description in the Crucirescu work [5].

2.5.2 Analyzes in the vegetable stew of type „Zacusca”

The preparation of the samples for analysis was carried out in the following way: the stew was homogenized in a mixer and diluted with distilled water of 19 ± 1 °C in a ratio of 1:5. The whole mass was heated in a water bath at 80 ± 2 °C for 30 min, then cooled to 20 ± 1 °C and filtered. The obtained supernatant was used for the necessary determinations.

The determination of total dry matter in the stew was carried out using the gravimetric method by drying in an oven at 103 ± 2 °C for 3 hours. The experiment was repeated until the mass became constant (AOAC,1999) [14]. Titratable acidity and chlorides were determined by direct titration of the analyzed supernatant with the sodium hydroxide solution in the presence of the phenolphthalein indicator (ISO 750:1998) [15], and with the standard silver nitrate solution in the presence of the potassium chromate indicator, based on the Mohr method, respectively. The ionic acidity was determined with a HANNA 211 pH-meter (Germany) the methods described in ISO 1842:1991 [16].

2.6 Sensory evaluation of Vegetable Stew of type „Zacusca”

Jars with the analyzed product were opened just before the sensory evaluation. Each taster was presented with a plate with equal amounts of vegetable stew, with equal conditions. The evaluation was carried out at a temperature of 19 ± 1 °C.

The 8 evaluators trained in the field of food technologies, aged between 35 and 75, participated as tasters. The following organoleptic indices were evaluated: appearance, color, smell, taste and consistency. The evaluation was carried out by both the descriptive and the scoring method, using the 5-point system, which includes the following scores: 5 - very good; 4 - good; 3 - satisfactory; 2 - unpleasant; 1- bad and 0 - very bad (ISO 6658:2017) [17].

2.7 Statistical analysis

Analysis of variance of the results was performed using one-way analysis of variance and Student's test. Microsoft Office Excel version 2010 software was used for statistical analysis. All analyzes were performed in triplicate with a maximum error of less than 5 %. The results obtained were expressed as mean \pm SD.

3. Results and Discussions

The acidifier from unripe apples *Golden Rezistent* variety harvested in 2019 on the 71st DAFB was obtained and can be seen in Figure 3. It was later analyzed physicochemically and sensorially in order to be applied to the production of vegetable stew type „Zacusca”.



Figure 3. Image of the experimental sample of acidifier from unripe apples *Golden Rezistent* variety.

The acidifier showed a clear liquid containing a straw-yellow sediment (less than 3 %). The taste was sour-sweet, with a light green apple flavor, pleasant, agreeable and balanced, specific to the apple variety. No foreign nuances were felt in the taste and smell. The juice yield after pressing to obtain the acidifier was 40-52 %.

The physicochemical indices determined in the studied acidifier are presented in table 2.

Table 2

The physicochemical indices determined in the apple acidifier

Characteristics	Results
Total soluble solids, %	8.47 \pm 0.10
Titratable acidity, %, expressed in malic acid	1.97 \pm 0.20
pH	3.01 \pm 0.10
Content of organic acids, g/dm ³ :	
Malic	32.95 \pm 0.01
Citric	0.26 \pm 0.01
Content of simple carbohydrates, g/dm ³ :	
Fructose	45.55 \pm 0.10
Glucose	23.51 \pm 0.14
Sucrose	0.07 \pm 0.01

The results in table 2 show that the acidifier from apples *Golden Rezistent* variety is characterized by an imposing amount of total soluble solids (8.47 %), high titratable acidity (1.97 %) and a low pH (3.01). The predominant organic acid, about 85-90 % of the total

organic acids in apples, is malic acid [18]. As expected, malic acid constituted the majority acid, having a concentration of 32.95 g/dm³, and citric acid was about a hundred times less (0.26 g/dm³). At the same time, the predominant carbohydrate was fructose with an amount of 45.55 g/dm³, and sucrose was presented as traces, registering values of 0.07 g/dm³. Glucose had a concentration about 2 times lower than fructose (23.51 g/dm³). The high amounts of carbohydrates are due to the process of photosynthesis, after which in the mesophyll of the leaves, sucrose and sorbitol are formed, which are transported to the unripe fruits for development [19, 20].

The impressive amounts of organic acids in apple acidifiers represent one of the promising ways to supplement the need for natural sources of acidity in the food industry. And significant amounts of carbohydrates can replace some of the sugar added to food during production. Marques et al. analyzed malic acid for its potential as a food ingredient [21]. Due to the penetration of organic acids into the cell wall, they have an antimicrobial and antibacterial effect [22]. At the same time, replacing chemical acidifiers with natural ones in production will improve the nutritional value of food [3].

Due to the need to implement natural sources of acidity in the food industry, the decision was made to apply the acidifier from apples to obtain vegetable stew of type "Zacusca", thus producing new functional foods.

The preparation of the mentioned stew was carried out according to the recipe and the production scheme presented in Table 1 and Figure 2, respectively. The experimental samples of elaborated products were obtained, in which quality indices were determined after 9 months of storage. Similar stew products from the normative document in force in the Republic of Moldova GOST 2654-98 (valid, according to OMAIA 153/2010) served as a reference [23]. The results of the analyzes are presented in Table 3.

Table 3

The physicochemical indices determined in the vegetable stew of type „Zacusca” samples

Characteristics	Norm *	Results
Total soluble solids, %, not less	18.0 – 27.0	27.0±0.05
Titrate acidity, %, recalculated to malic acid	n/n	0.42±0.04
Content of chlorides, %	1.2 – 1.6	0.94±0.07
pH	n/n	4.81±0.02
Impurities, including mineral	n/a	n/d

Note: * according to [23]; n/n – not normed; n/a – not admitted; n/d – not detected.

The results obtained in the determined samples show that vegetable stew of type "Zacusca" is very beneficial for consumption by the population, from the point of view of the composition, but also of the method of preparation, being the most requested. The amount of TSS had a high value, compared to similar products according to the norm 27.0 %, and the salt content, on the contrary, was lower, having 0.94 %. These results may be due to the fact that the apple acidifier contains its own TSS in significant amounts [2], there by increasing the TSS content of the finished product. Salt, however, was added in minimal amounts in the production process. The total concentration of organic acids and pH were 0.42 % and 4.81, respectively, which confirms that the developed food product can be acceptable to all consumers. Acidity affects both the taste and aroma of the finished product, as well as microbial stability and shelf life [24].

Sensory analysis of the food product is carried out for a wider understanding of it. Vegetable stew of type "Zacusca" was evaluated by the tasting committee composed of 8 people trained in the field of food. All the evaluators were pleasantly surprised by the results obtained, especially by the aroma and taste of the grilling smoke. At the same time, a slight separation of the liquid from the entire mass was observed, which is allowed in the case of boiled or baked vegetable stew, according to GOST 2654-98 (OMAIA 153/2010) [23]. The description of all sensory characteristics is presented in Table 4.

Table 4

Descriptive analysis of the vegetable stew of type „Zacusca” samples	
Characteristics	Description *
Appearance	Eggplant paste with inclusions of pieces of eggplant and red bell peppers cut to almost the same size, possible inclusions of tomatoes, all skinless. The presence of soft eggplant seeds evenly distributed throughout the mass, a slight separation of the liquid from the entire mass.
Color	Characteristic of canned vegetables, without burns. The pieces of pepper and tomato have a homogeneous red color, eggplant - light-brown. The color of the mass – red-orange to brown.
Smell and taste	Characteristics of heat-treated vegetables, very pleasant and well expressed, with a shade of smoke, without bitter taste and foreign nuances.
Aroma	Pleasant, with a slight shade of green apple and cooking smoke.
Consistency	Zacusca is presented in the form of a paste with inclusions of pieces of eggplant, bell peppers and tomatoes. Vegetables well processed, soft, but not overcooked.

Note: according [25] * descriptive method, according to ISO 6658:2017.

Following the sensory evaluation (Table 4) it was concluded that all 5 analyzed indicators presented very good results. The products did not present any objections from the tasting committee and were appreciated with maximum points. At the same time, for a more complex understanding, in figure 5 are presented the photos of the exterior aspect of the elaborated product.



Figure 5. Image of the experimental sample vegetable stew of type „Zacusca”.

Conclusions

Golden Reizistent apples harvested on the 71st DAFB served as raw material for obtaining the natural acidifier. It was characterized by high values of titratable acidity (1.97 %) and of TSS (8.47 %). As expected, malic acid was the predominant organic acid with the concentration of 32.95 g/dm³, and fructose was the main carbohydrate with 45.55 g·dm⁻³. Glucose showed a value about 2 times lower than fructose (23.51 g/dm³). Citric acid and sucrose were found in very small amounts with the content of 0.26 g/dm³ and 0.07 g/dm³, respectively. The pH value of the acidifier was 3.01.

The studied apple acidifier was applied to the production of vegetable stew of type "Zacusca", in laboratory conditions, with the elaboration of the recipe and the production scheme. The experimental stew samples had better physicochemically characteristics compared to similar products, according to the normative documentation in force. The amounts of titratable acidity and salt were low, with values of 0.42 % and 0.94 %, respectively, and the TSS content was significant (27.0 %). The developed product was appreciated with maximum score by the tasting committee for all 5 sensory indices.

The use of unripe apples, being horticultural waste, with the obtaining of the natural acidifier and its implementation in the food industry, is a key factor for the development of new healthy foods with a high nutritional value.

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Conflicts of Interest. The author declares that they have no conflict of interest.

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