NATURAL ACIDULANTS FROM GRAPE

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Abstract: Non–alcoholic products from grape are proposed, as alternative of use for Vitis Labrusca varieties, which actually are not asked in winemaking. A processing direction may be the production of natural acidulants that can substitute chemical organic acids in various foods. The results of investigations prove what technological process was applied in juice making and how vary during ripening the sugars content in relation with total acidity, sugar/acidity ratio in juice Noah and Isabella varieties is determined in dynamic. Organoleptic and more representative physical–chemicals indices were established in acidulants samples. Canned fruits and vegetables which citric and acetic acids were substituted with grape acidulant, were produced in laboratory conditions. It is decided what successful are fruit puree and canned vegetables. Now it works to optimize the production processes.

Key words: Grape, natural acidifiers, non–alcoholic products.

Introduction

Non–alcoholic products from grape Vitis Labrusca varieties – Noah, Isabella, Lidia, is proposed to obtain for industrial use of large harvest quantities which actually are not asked in winemaking. Research results prove the detailed production of acidulants and juices with moderated acidity that can be used in canned vegetables and fruits.

Actually, organic acids as citric, malic, fumaric, acetic, etc. are employed to acidify drinks, purees, culinary, canned, many of them are of chemical origin. Research projects are known to obtain natural acidulants.

Ojeda H. et al., at the National Institute for Research in Agronomy in partnership with Foulon Sopagly (France) studied ways to diversify wine products, they obtained a product called "verjus" possessing high acidity, low content of sugars and pronounced aroma of green grapes [1].

Troyan Z. and colleagues at the Research Institute for the storage and processing of agricultural production in Krasnodar (Russia) have proposed the use of fruit juice from white plum in canned vegetables as a substitute for acetic acid [2].

Was studied the possibility of making new foods from Vitis Labrusca grapes harvested in various stages of maturation, without involving fermentation to making, with optimization of technologic process to produce acidulants from immature grapes, in order to use in industrial conditions.

Materials and methods

Grape of Noah and Isabella varieties harvested for August–September period of year 2013, was used as a raw material to produce juice samples. Titratable acidity expressed in g/l of tartaric acid was determined by titration with NaOH 0.1N alkaline solution up to the slight pink tint. The content of glucose and fructose was determined by high–performance liquid chromatography (HPLC) in accordance with Resolution Oeno

23/2003. 25ml juice samples were filtered through blocks of 0.45–0.8–1.2–5μm filters + pre–filter and were 5–time diluted by homogenization of 20ml of juice with 80ml of distilled water in 100ml measuring flasks. 9ml of every diluted solution of juice were passed through filtering cartridge with last 6ml transferred into the test glass. Mobile phase – acetonitrile: water isocratic eluent in 85:15 ratio; flow rate – 1ml/min; temperature in column +20°C. Initially, 10μl standard solutions of fructose, glucose and saccharose of 5g/l concentration each were introduced. Then, 10μl work juice solutions prepared of grape of different phases of ripening were introduced. Solutions were kept in Zorbax–NH_2 150x4.5 column for some period specific for every substance. Quantitative analysis was carried out using refractometric detector.

The content of malic, tartaric and citric acids was determined by high–performance liquid chromatography (HPLC) in accordance with OIV General Methods. 20ml juice samples were degassed and then filtered through 0.45μm cellulose membrane + pre–filter. 8ml of every juice solution were passed through filtering cartridge with last 5ml transferred into the test glass.

Mobile phase – eluent solution of 0.0035M sulfuric acid; flow rate – 0.5ml/min; the temperature in chromatographic column +20°C. Initially, 10μl standard solutions of malic, tartaric and citric acids were introduced. Standard solutions had following concentrations: malic acid – 0.8 g/l; tartaric acid – 2.5 g/l; citric acid – 0.6 g/l. Then, 10 μl work juice solutions prepared of grape of different phases of ripening were introduced. Acids were kept in Zorbax Sax 250x4.6 mm column for some period specific for every substance. Quantitative analysis was carried out using diode–array detector (DAD) at 192, 208 and 210nm wavelengths.

Results and discussions

In August–September period of the year 2013 grape of „Vitis Labrusca" varieties Isabella and Noah were harvested at different stages of their ripening, from trial plots of the National College of Viticulture and Winemaking „Stauceni".

Soluble dry substances and titratable acidity were determined from every batch of fresh harvested grape, then juice samples were obtained according to the technologic process as follows.

Technologic process to produce experimental samples of grape juice

Received grapes were inspected and graded, washed with fresh water, the pressure being of 1.2–1.3 atm., then blanching followed for 2–3 min. with hot water at a temperature of 80°C. The blanched grapes were destemmed and crushed; obtained must was treated with pectolytic enzymes at a temperature of 40–42°C for 10 min, and then pressed. The juice obtained at the pressing was settled and then filtered. Heat treatment was carried out at 85°C, the duration was established according to the raw material type: 20 min. for grape juice with titratable acidity 2.0–2.5% and 25 min. to that obtained from grape with acidity 1.2–2.0%. Heat treatment conditions are easier because juice pH values were 2.5–3.0, conditioned by acids content with preservative effect.

First variant provided after heat treatment the pouring of hot juice in jars and their sealing with Twist–off caps.

Second variant provided after heat treatment the cooling of juice to a temperature of 4°C and maintaining at this temperature for 48 hours to sediment tartrates. For the

separation of the formed crystals, the juice was decanted and then directed to the concentration at 50°C and a pressure of 720±20 mm Hg, till it obtained 30–32% soluble dry substances. Concentrated juice poured into Twist–off glass jars with 380 to 560 ml volume.

Juice samples were given to organoleptic appreciation and physical–chemical analysis in order to determine the organic acids, sugars and polyphenolic substances.

As acidulants were determined to be grape juice with index sugar/acidity that has values within the limits of 4–8 units, and juices with moderate acidity within limits 8–12 units.

Sensorial analysis

Noah variety juice containing soluble dry substances of 13.5% and titratable acidity of 1.9% is clear, straw yellow with slight haze. Taste is acid, pleasant, agreeable, specific variety. Aroma is pleasant, slightly expressed, characteristic Noah variety. The precipitate is accepted.

Isabella variety juice containing soluble dry substances by 14% and titratable acidity of 1.75% is a clear, pale pink, with slight haze. Taste is more intense than that obtained from variety Noah, agreeable, specific variety. Aroma is pleasant, slightly expressed, characteristic Isabella variety. The precipitate is accepted.

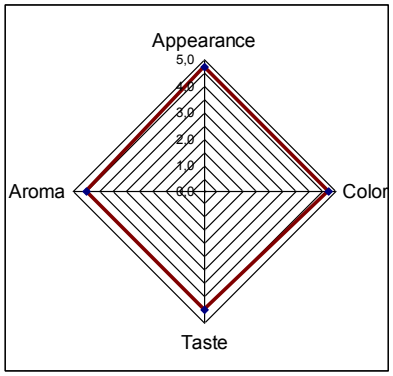

Fig. 1 Organoleptic appreciation of acidulant from grape variety Isabella

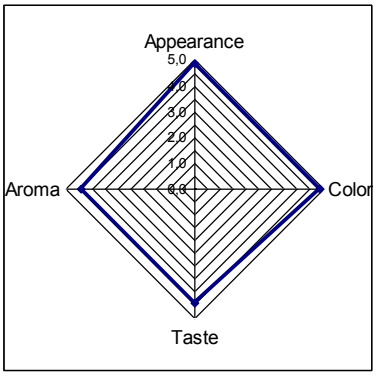

Fig. 2 Organoleptic appreciation of acidulant from grape variety Noah

Data are obtained concerning total content of sugars and titratable acidity, then index sugar/acidity was determined in samples of juices Noah and Isabella varieties (figures 3 and 4).

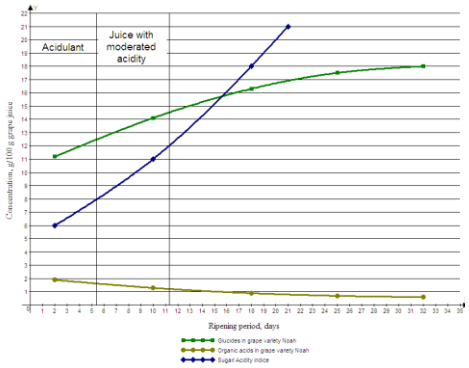

Fig 3. Sugars/organic acids ratio in grape variety Noah during the ripening

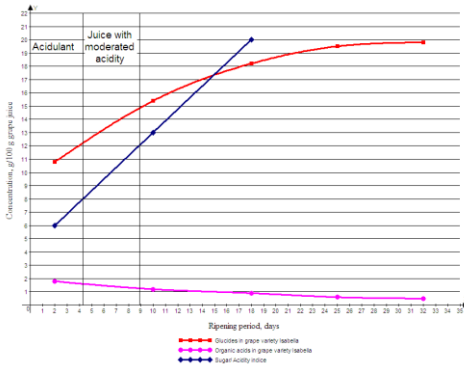

Fig. 4. Sugars/organic acids ratio in grape variety Isabella during the ripening

From figures 3 and 4 are observed during the investigations an increase in the sugars content and decreasing organic acids, similar to the results obtained Sabir and colleagues at cultivated varieties in Turkey [3], a phenomenon that corresponds to the studies concerning main nutrient metabolism in the grapevine plants, made by Ribereau–Gayon and Peynod [4]. Based on these two parameters, the index sugar/ acidity was calculated and indicated on the graphs, were defined conventional phases to collect grapes for producing various products. Thus, the first harvest of 15 August is best to obtain acidulant, the second to make juice with moderate acidity, while the other three are at the stage of full maturity and can be directed to processing to get the juice according to classical technology.

By high–performance liquid chromatography (HPLC) were determined the main representatives of organic acids and sugars in the grape juice, and by UV–VIS spectrophotometry was determined the content of polyphenolic substances (IPT), during the maturation study of 30 days.

Table 1. Organic acids, sugars and polyphenolic substances in grape juice varieties Vitis Labrusca

Grape juice	Sugars, g/100g juice			Organic acids, g/dm^3 juice				IPT, mg/L	Harvesting date
	Glucose	Fructose	Total	Malic	Tartaric	Citric	Total		
Noah	5,86	4,98	11,23	9,35	8,89	0,83	19,15	290	07.08.2013
	6,91	7,05	14,11	6,42	6,16	0,57	13,22	340	15.08.2013
	8,06	7,89	16,34	4,31	4,45	0,30	9,08	460	23.08.2013
	8,57	8,64	17,47	3,25	3,38	0,25	6,97	510	30.08.2013
	8,95	9,00	18,09	2,84	2,93	0,23	6,05	530	06.09.2013
Isabella	5,33	5,16	10,78	9,22	8,35	0,49	18,07	580	07.08.2013
	7,52	7,24	15,39	6,43	5,29	0,42	12,16	720	15.08.2013
	8,89	9,10	18,17	4,15	4,76	0,38	9,21	950	23.08.2013
	9,32	9,86	19,46	2,73	3,10	0,24	6,15	1390	30.08.2013
	9,17	10,35	19,82	2,41	2,65	0,20	5,34	1540	06.09.2013

The data in Table 1 demonstrates that the main sugars in grape juice are glucose and fructose, which accumulate in almost the same proportions, only to full ripeness fructose prevail. Most significant organic acids are malic, tartaric, citric, their amounts decrease during ripening, the malic acid content to the end decreases more intensely than that of tartaric acid. Polyphenolic substances accumulate more in red variety Isabella than in white variety Noah, but we see that in the early phase are quantities that present interest from nutritional standpoint.

Therefore it can be shown that the production of acidulants is sufficient that the grape of Vitis Labrusca varieties contain from 10% to 14% soluble substances, at this stage they have 7–12,5% sugars and have titratable acidity of 1.2 to 2.5%, polyphenolic substances accumulate 200–320 mg/dm^3 in white varieties (Noah) and 500–700 mg/dm^3 in red varieties (Isabella).

In comparison with organic acids used for drinks, puree and canned grape acidulants have higher nutritional value and are natural.

It is important that harvest period of grape for acidulants production be established depending on physical–chemical composition and optimum organoleptic indices.

We obtained experimental samples of canned fruits and vegetables, where we substituted in the recipe citric and acetic acids with acidulants from Noah and Isabella grape variety with 20%, 30% soluble substances (concentrated version), see table 2.

Table 2. Canned with acidulants from grape varieties Vitis Labrusca

Order	Experimental samples of canned with natural acidulant from grape	Organoleptic appreciation, points			
		Appearance	Color	Taste	Aroma
1.	Green nut jam (ac. Noah)	4,3	4,2	4,1	4,0
2.	Red cherry compote (ac. Isabella)	4,6	4,5	4,2	4,2
3.	Peach puree (ac. Isabella)	4,6	4,6	4,3	4,2
4.	Canned sweet pepper (ac. Noah)	4,5	4,4	3,9	4,0
5.	Canned tomato (ac. Isabella)	4,6	4,5	4,3	4,4

Relatively successful samples were the peaches puree and canned tomato with acidulant from grape Isabella variety, but more research is required to find balanced ratio of components and develop an optimized technology.

It was decided to work specifically with purées of vegetables to compensate the acidity deficiency for canned carrots, pumpkin, beetroot, etc.

Conclusions

1. Were studied Noah and Isabella grape varieties during their maturation, and were established optimal characteristics for natural acidulants.
2. Canned obtained using natural acidulants demonstrate relevant organoleptic indices that characterize the perfect blend of acidulant with product matrix.

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