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PROCESSING AND CHARACTERIZATION OF SOME FLAVORED VINEGARS

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Abstracts

In this paper was obtained apple vinegar that was flavored with spicy plants mixture and different fruits in the view to improve the organoleptical and chemical properties. The obtained vinegar types were analyzed for some physico-chemical characteristics (organoleptical features, total acidity, extract, sediment-determined on the basis of standardized method) and antioxidant activities (using FRAP method), total polyphenols amount (by Folin-Ciocalteu method) and ascorbic acid content (using 2,6-dichlorophenol indophenol method). The antioxidant capacity varied between 4.5-5.5 mM Fe^{2+}/L for apple vinegar flavored with spicy plants and between 4.5-7.7 mM Fe^{2+}/L for vinegar flavored with fruits. By flavoring of apple vinegar with fruit the polyphenols content increases with 13-32% in rapport with apple vinegar; for apple vinegar flavored with spicy plants the increasing of polyphenol content is insignificantly. The values obtained for ascorbic acid content was situated between 0.5-2.2 mM/L, different for analyzed apple vinegar and apple flavored vinegar.
***Key words**: apple vinegar, flavored vinegar, antioxidant capacity, polyphenols, ascorbic acid.*

Introduction

The word *vinegar* is from the Greek word *okijus.* As raw material are used alterated wines and those with little alcohol obtained from cereals, potatoes, fruits juices, syrups, other materials with starch etc. Usually are used acid wines; the bitter ones are not used because their smell is stronger. Alcohol content mustn’t be too high; the optimal content is 8-9%. Before acetic fermentation wines must be filtrated, this operation being one of the most important for clearing. In the countries where grapes production is small, vinegar is fermented on malt, cereals and beer. The products obtained have a fade taste, not pleasant and without smell. To improve these characteristics is added some wine.

Different species of bacteria have different behavior in acid presence. The introduction of acid resistance bacteria will allow obtaining selective conditions to protect production process on not desirable flora.

Prepared after a good technology, vinegar could be good in some diseases. Optimal temperature of fermentation is between 20-30°C, the whole process being in an open glass, ceramics or wood recipient. In order that fermentation is normal, all recipients mustn't be exposing on sun, because UV radiation don't permit fermentation. The process is final when the liquid is clear, after 40-60 days, after that obtained vinegar is filtered (Jianu, 1998).

From a biochemical viewpoint, apple vinegar is the next step after (apple wine) cider itself on the road which converts sugar through to alcohol, thence to acetic acid and finally to carbon dioxide and water. At each step, the organisms involved gain energy - this, after all, is why they do what they do and their metabolism is very little different from our own in many respects. Animals, however, do not stop at the alcohol or acetic acid stage. Some micro-organisms do and we can take advantage of this to provide the products that we want.

Vinegar is simply a dilute solution (about 5%) of acetic acid which has been converted from a corresponding quantity of alcohol. To make cider vinegar we need to start with a fully fermented dry cider with a minimum 5% alcohol content. Sulphur dioxide should not have been added, because this will inhibit the conversion to acetic acid. Contrary to all good cidermaking practice, we then need to leave the cider in a vessel with plenty of access to air and to ensure that *Acetobacter* can get in.

The measurement of total antioxidant capacity (TAC) can be making using different methods (photometric, chemiluminescence's and spectrophotometric methods) (Kalt, 1999; La Vecchia, 2001; Mannino, 1998; Proteggente, 2002; Richelle, 2001).

On the basis of the mentioned data in literature and on the experience of the authors regarding the determination of antioxidant capacity, we chose the modified method FRAP. This method it was based of the ability of antioxidant substances present in analyzed juices to reduce the ferric ions (Fe^{3+}) from tripyridyltriazine complex to the ferrous ions (Fe^{2+}). The ferrous tripyridyltriazine complex has an intensive blue color and can be monitored at 593 nm (Benzie & Strain, 1996).

This method is properly in the case of total antioxidant capacity determination for different natural products (Ou, 2002; Pellegrini, 2000; Pellegrini, 2003; Gergen, 2004). For polyphenols determination (expressed such as mM/L acid galic) will be use the spectroscopic method with the Folin Ciocalteu reactiv (Folin, 1927; Simonetti, 1997; Terry, 2001; Vinson, 1998; Gergen, 2004).

Experiental

Reagent and equipment: All chemicals and reagents were analytical grade or purest quality purchased from Merck, Fluka, Sigma. Was used distilled water. Absorption determination for FRAP and total phenol content was made using Spectrophotometer Specord 205 by Analitik Jena.

Obtaining of apple vinegar and flavoured vinegar: For obtaining apple vinegar, apples are washed, damaged parts are taken away and then fruits are cut and are used all parts. Could be used all parts remains from fruits canning. All cut apples are put in a proper recipient; on fruits is pored warm water, which before was boiled (0.5L water to 0.4kg apples). For every L of water is added 100g honey or 100g sugar. To accelerate acetic fermentation, on each L of water is added 120g yeast and 20g black bread. The recipient with this mixture is storage in a room at 20-30°C.

Acetic fermentation is favored by a small alcohol content liquid (bellow 20% sugars), a constant temperature of 20°C and a big contact area of mixture with air (aerobe fermentation). The recipient is from glass, wood or ceramics.

For the first phase of fermentation the recipient is stored in a warm environment for 10 days at 20-30°C, mixing twice a day, and then is filtered by pressing. Obtained juice is filtered again; the volume is measured and is stored in a recipient with a big contact area with air. If it's necessary is added 50-100g honey or sugar for every L of juice and it's very good homogenized.

For the second phase of fermentation the recipient is stored in a warm place to continue the fermentation. The fermentation is finished when the liquid is clear.

Depending on juice preparation, temperature, etc the vinegar will be done in 40-60 days. After that vinegar is filtered, bottled, waxed and stored in a cool place (4-10°C).

<u>Apple vinegar amortization with spicy plants</u>: Mixture I: 2g parsley, 1g savory, 0.5g tarhon. Mixture II: 0.5g dill, 1g laurel, 2g piper. 300mL apple vinegar is mixtured with each plant mixture. It is stored in glass with top recipients, it is kept for 30 days, is filtered and stored in glass closed recipients at 4-10°C.

<u>Apple vinegar amortization with fruits</u>: 300mL apple vinegar is separately mixtured with 75g fruits (red oranges, kiwi, raspberry, and grapefruit). The way of making is the same above.

Determination of Total Antioxidant Capacity (Adaptation of FRAP method): Reagents: acetate buffer, 300 mM/L, pH = 3.6 (3.1 g sodium acetate $3H_2O$ and 16 mL conc. Acetic acid per 1L off buffer solution); TPTZ (2,4,6-tripyridyl-s-triazine) solution 10 mM/L (0.31 g TPTZ in 100 mL HCl).

Prepared freshly always utilization; $FeCl_3$ solution 20mM/L (0.54 g $FeCl_3 \cdot 6H_2O$ in 100 mL distilled water). Prepared freshly always utilization; FRAP working solution (25 mL acetate buffer, 2.5 mL TPTZ solution, 2.5 mL $FeCl_3$ solution). Prepared freshly always utilization; Standard solution - Mohr salt 1mM/L.

Aqueous solution of known Fe concentration was used for calibration, in a range of 0.1-0.8 mM/L. For the preparation of calibration curve 0.5 mL aliquot of 0.1, 0.2, 0.4, 0.6, 0.8 μM Fe^{2+}/mL aqueous as Mohr salt solution were mixed with 2.5 mL FRAP working solution. FRAP reagent was used as blank. One mL from diluted 1/10 vinegar was mixed with the same reagents as described above, and after 10 min. absorption was read after at λ= 593 nm. The Total antioxidant capacity in fruit juices and fruit nectar in Fe (II) equivalents was calculated. Correlation coefficient (r^2) for calibration curve was 0.998.

Determination of phenolic compounds: The content of total polyphenolic compounds was determined by Folin-Ciocalteu method. Reagents: Folin-Ciocalteu′s phenol reagent solution 1:10; Na_2CO_3 solution 7.5%; Standard solution - Gallic acid 10mM/L.

For the preparation of calibration curve 0.5 mL aliquot of 0.2, 0.3, 0.4, 0.8 and 1.2 μM/mL aqueous gallic acid solution were mixed with 2.5 mL Folin-Ciocalteu reagent and 2.0 mL sodium carbonate. One mL from diluted 1/10 vinegar was mixed with the same reagents as described above, and absorption was read after 2 h at λ= 750 nm. Total content of polyphenols in fruit juices and fruit nectar in gallic acid equivalents (GAE) was calculated. Correlation coefficient (r^2) for calibration curve was 0.995.

Determination of ascorbic acid: Ascorbic acid content was estimated titrimetrically with 2,6-dichlorphenolindophenol natrium dye reactant. 10 mL of vinegar(diluted 1/10) with 10 mL distilled water and 1 mL HCl 1N it was titrate with 2,6-dichlor-phenolindophenol natrium to pink color. On the basis of 2,6-dichlorphenolindophenol natrium volum it was determined the ascorbic acid content (Szeto, 2002; Gergen, 2004).

Results and Discussions

The organoleptical characteristics of apple vinegar flavored with spicy plants is showed in the Table 1 and for apple vinegar flavored with different fruits is presented in the Table 2. The results from these tables showed that the color, the taste, the smell and the aspect of apple vinegar is substantial modified by flavoring.

The chemical characteristics (total acidity, extract, sediment-on the basis of STAS 157-86, total antioxidant capacity – TAC, Ascorbic Acid and polyphenols) are presented in Table 3 for apple vinegar flavored with spicy plants and in Table 4 for apple vinegar flavored with different fruits.

The apple vinegar flavored with fruits presents TAC more apple vinegar flavored with spicy plants. The same variation was observed for total polyphenols and ascorbic acid. For apple vinegar flavored with fruits nectar, the highest polyphenols amount was found in the case of vinegar flavored with raspberry and the smaller in the case of apple vinegar flavored with grapefruit.

In all situations, by flavoring the TAC, total polyphenols and ascorbic acid is increased, in more measure in the case of flavoring with fruits and in a small measure in the case of flavoring with spicy plant. The explication is that the fruit added for flavoring have the increased polyphenols content and also. The antioxidant capacity and ascorbic acid comparatively with used plants.

For apple vinegar flavored with fruits the ascorbic acid content is highest in the vinegar flavored with kiwi, and the minim value in the case of vinegar with red orange. in apricot and cherry. In the case of vinegar flavoured with spicy plant, the increase of ascorbic acid content, was 5% reported to apple vinegar.

Table 1. Organoleptic properties of apples vinegar aromatized with spicy plants

Charact eristics	Kind		
	Apple vinegar	Plant aromatized vinegar (I)	Plant aromatized vinegar (II)
Aspect	Clear liquid without strange corps	Clear liquid without strange corps	Clear liquid without strange corps
Color	cognac	Orange-brown	Orange-scarlet
Smell	Characteristic of apple vinegar	Characteristic of used mixture, tarhon	Pleasant, characteristic of used mixture, without any particular smell of used plants
Taste	Sour, characteristic of apple vinegar	Sour, with taste of tarhon and savory	Sour, spicy because of piper

Table 2. Organoleptic properties of fruits aromatized apple vinegar

Characteristics	Kind				
	Apple vinegar	Aromatized vinegar with red oranges	Aromatized vinegar with kiwi	Aromatized vinegar with raspberry	Vinegar aromatized with grapefruit
Aspect	Clear liquid without strange corps	Clear liquid without strange corps	Liquid without strange corps slab opalescent	Clear liquid	Less opalescent liquid
Color	cognac	Orange with red pales	Brown, with green pales	Scarlet	Yellow with orange reflexes
Smell	Characteristic of apple vinegar	Characteristic of citric	Pleasant, of kiwi	Characteristic, with raspberry smell	Specific, of citrics
Taste	Sour, characteristic of apple vinegar	Sour, with pleasant pales of tarhon and savory	Sour, spicy because of piper	Sour, aromatized with raspberry	Sour, specific of grapefruit

Table 3. Chemical properties of apple vinegar flavored with spicy plants mixture

Chemical characteristics	Vinegar type		
	Apple vinegar (AV)	AV + plants (I)	AV +plants (I)
Total acidity (g acid acetic/100 mL)	5.19	5.32	5.27
Extract (g/100 mL)	8.5	8.62	8.8
Sediment (g/L)	0.17	0.184	0.191
Ascorbic acid (mmoli/L)	0.162	0.166	0.171
Antioxidant capacity (mM Fe^{2+}/L)	4.5	5.27	5.49
Poliphenols (mM acid gallic/L)	4.92	4.97	4.93

Table 4. Chemical properties of apple vinegar flavored with different fruits

Chemical characteristics	Vinegar type				
	Apple vinegar (AV)	AV+red orange	AV+ kiwi	AV+ raspberry	AV+ grapefruit
Total acidity (g acid acetic/100 mL)	5.19	4.05	4.69	4.43	4.27
Extract (g/100 mL)	8.5	11.5	12.7	11.9	12.3
Sediment (g/1000 mL)	0.17	0.247	0.292	0.264	0.285
Ascorbic acid (mmoli/L)	0.162	0.197	0.227	0.203	0.219
Antioxidant capacity (mM Fe^{2+}/L)	4.5	5	4.74	7.68	6.14
Poyphenols (mM acid gallic/L)	4.92	6.31	5.95	6.48	5.56

Conclusions

The apple vinegar flavored with fruits were presented more total antioxidant activity, polyphenols and ascorbic acid content than apple vinegar flavored with spicy plants.

The results of this paper show that, the flavoring with fruits is a very good method for improve of organoleptical features and for increasing of antioxidant capacity of apple vinegar. By apple vinegar flavouring with spicy plants mixture not were significantly modified the chemical properties but were observed the important changes of organoleptical characteristics, in specially the taste and smell.

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