Determination of biogenic amine content of Tokaj Wine Specialities

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Summary: The knowledge of the finest composition of the Tokaj Wine Specialities is an indispensable task. The presence of the biogenic amines as an eventual combination of hygiene, technology and activity of *Botrytis cinerea* is a very important point of view in the future. The objective of this study was to measure the biogenic amine-content of Tokaj Wine Specialities.
According to our findings, the histamine-concentration remained lower than the prescribed end values, but in the case of serotonine, there were significant measured values. During the fermentation period, in the first cycle there was a decrease in the concentration of biogenic amines, but with the advancement of fermentation, an increase was found.

Key words: biogenic amine, Hungarian Wines, Tokaj Wine Specialities

Introduction

Tokaji Aszú was called to be „the Wine of Kings, the King of Wines" by Louis XIV. The phrase of „Tokaji wine is bannered with flag" is often used when we talk about wines from Tokaj Region and about Tokaj Wine Specialities.

The unique feature of Tokaj Wine Specialities is determined by the „Aszú-character" derived from noble rot and by the „Tokaj-character" which comes from ageing.

It is very important to mention that the two main characters of Tokaj Wine Specialities are proper only when the grapes are in mature or overmatured state and we have to pay attention to the other requirements such as grape-variety, soil, year and climatic condition.

The „Aszú-character" and „Tokaj-character" have been determined on an organoleptic base so far, but there is an obvious need to determine compounds identified chemically to fortify the main characters mentioned above. The aim is to determine chemically identifiable compounds, so in this study we show the results in our measurings of the biogenic amine-content.

In our earlier work we have studied the biogenic amine-content of Hungarian wines and champagnes (Kállay et al., 1981). At present, Simonné et al. regularly measure the biogenic amine-content of wines. They widen our knowledge on amine-values of domestic wines *(Simonné & Csomós,* 1999). They have measured for example the amine- and aminoacid- composition of Tokaj Wine Specialities *(Simonné & Csomós,* 2002). In wines, the formation of biogenic amines is realized by the decarboxylization of aminoacids. Concerning physiological effect, histamine (allergic compound of hypotension), tiramine (compound of hypertension) are the most important biogenic amines. Histamine is derived by histidine-decarboxylaze enzyme. Tiramine is formed from the decarboxylization of tirozine aminoacid *(Kállay,* 1991).

Serotonin is an other important biogenic amine, it has got an essential effect on regulating the blood pressure, futhermore it can be a medicine in case of depression-maladies. The first determination of serotonin-content in wines has been realized by us.

The following wine categories make up the groupe of wine-specialities: Tokaj Szamorodni (dry and sweet), Tokaj Máslás, Tokaj Fordítás, Tokaj Aszú Wine (3–6 butt), Aszúeszencia and Tokaj Eszencia (Nectar).

After the noble rotting process, the composition of grape-juice and wine is changed *(Figure 1).*

Experimental goals

During our work, we have searched the answers for the following questions:

1. Change in the composition and concentration of biogenic amines during the fermentation in normal must
2. Study of the amine-composition of noble rotted berry-extract
3. Change of biogenic amines in the year of 2002 in Tokaj Wine Specialities made from different aszú-berries
4. Amine-composition of Tokaj Wine Specialities from different years.

Changes in the composition of must	The effect of changes on the wine
DECREASE	
vintage quantity	
juice gaine	
sugar →	glucose-fructose ratio of residue
glucose-fructose ratio	sugar-content under 1
tartaric acid	
malic acid	
aminoacids	slow fermentation
vitamins (tiramine)	increase of higher alcohols
(pectine)	mucus acid, mucus acidous calcium, higher methanol-content
INCREASE	
relative sugar-content	slow fermentation
glycerine 5-10 g/l	increase in the wine too, >10 g/l
gluconic acid >5 g/l	it is not fermented by yeasts, it is unchanged in wines
citric acid, succinate acid	special acid-composition
ketoneacids (pyroracemic acid,	combined sulphurous acid-quantity increases
2-ketoglutaric acid)	
poliphenoloxidases	inclination to get brown, oxidatic casse
polisaccharides (ß-glucane)	poor filterability

Figure 1 The effect of *Botrytis cinerea* on the composition of grape-juice and wine

Material and method

Samples

1. Tokaji Furmint-must from 2002
2. Noble rotted berry-extracts
3. Raw aszú-wines
4. 150 pieces of aszú wines with different butt-numbers

Manner of measuring

Biogenic amine – content of wines was determined by High Performance Liquid Chromatography. The chromatographic conditions were the following:

Type of equipment: HPLC typed HP 1050

Column: Nukleosil C-18

Detector: Fluorescent detector, HP 1046 A type

Liquid-flow: 1 ml/min

Temperature: 30 °C

λ_{ex}: 340 nm λ_{em}: 440 nm

Composition of eluent: A – solution: 0.08 M acetic acid
B – solution: Acetonitrile

The efficiency of reversed phase chromatographic segregation was enhanced with gradient elution techniques. The gradient composition, its running in time are shown in *Table 1.*

The identification of components was realized by standards (SIGMA and FLUKA), the concentration of components was measured by calibration lines with standards.

Table 1 Gradient – composition

TIME (min.)	A%	B%
3.5	70	30
10	35	65
21	28	72
22	20	80
25	20	80
30	70	30

Preparation of wine-samples

Each wine was filtered by membrane filter (0,45 µm), then reacted with orto – phtalaldehyde (OPA) reagent in borate-buffer according to below:

- 0.5 ml of borate-buffer: 0.5 g H_3BO_3 dissolved in 19 ml of distilled water, then setting the pH to 10.4 with KOH –solution concentrated 40 g/100 ml
- 0.1 ml of OPA reagent (SIGMA)
- 0.1 ml of wine-sample

20 µl of prepared wine-sample was injected into HPLC – equipment after a reaction time of 2 minutes.

Preparation of aszú-berries

10 g of noble rotted berries was pounded in a mortar avoiding the hurt of soils, then mixed with 50 ml of methanol (50%). After one hour of waiting, the mixture was filtered and completed to 50 ml. The results were counted in mg/kg aszú-berry.

Results

We measured the biogenic amine-composition every day during the fermentation period in Tokaji Furmint musts. There were a spontaneous must and two musts inoculated with different specified yeasts. The same run could be observed in the three cases but with different intensity. The tiramine, serotonin and total biogenic amine quantity of the three samples running in time are shown in *Figure 2,3,4.* The amines were used as nitrogen-sources by yeasts in the first period of fermentation, it is shown in the initial

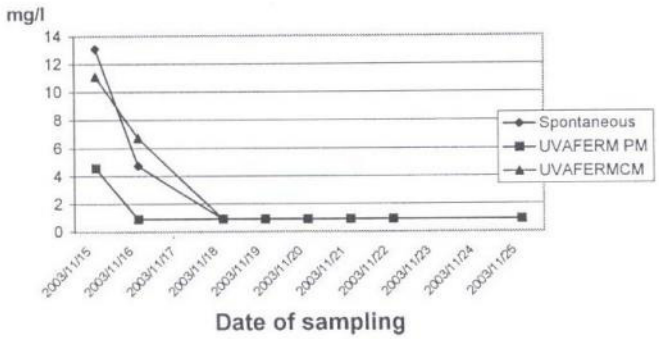

Figure 2 The change of tiramine content during the fermentation

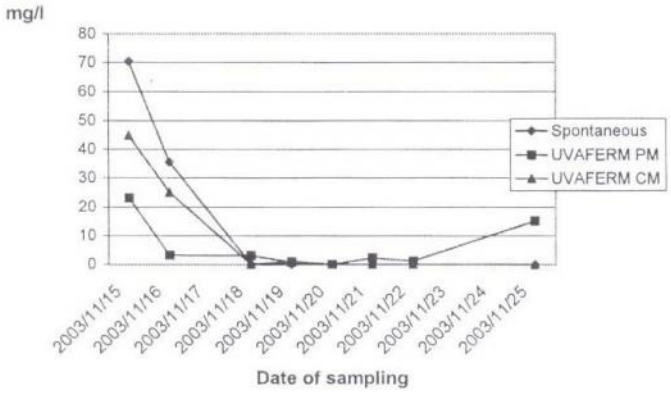

Figure 3 The change of serotonine content during the fermentation

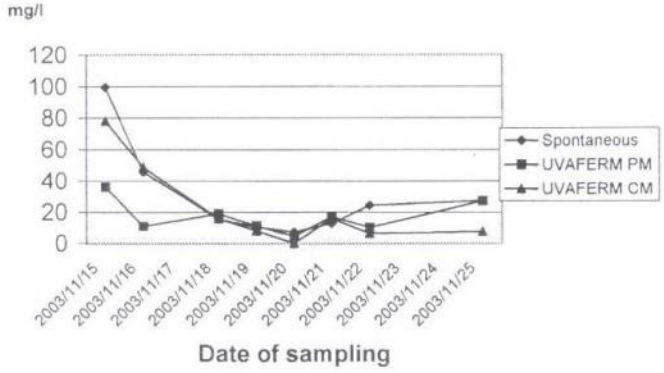

Figure 4 The change of total biogenic amine content during the fermentation

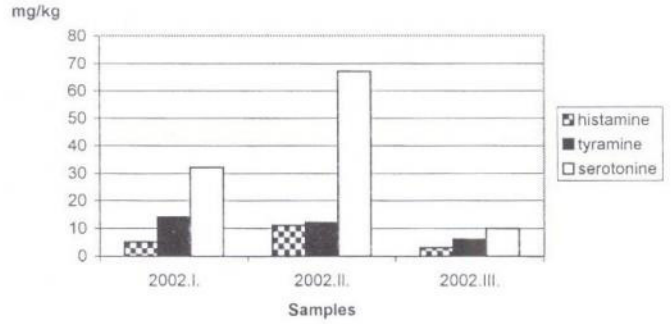

Figure 5 The histamine, tyramine and serotonie content of aszú berry extracts

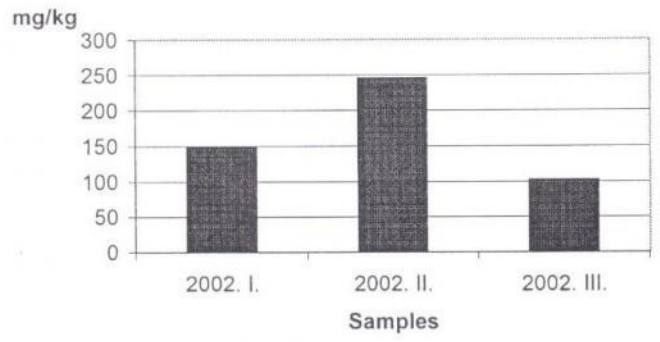

Figure 6 The total biogenic amine content of aszú berry extracts

decreasing part of the Figures. In this way the initial biogenic amine-concentration of musts decreases during the fermentation. There is a certain increase what can be measured in the end of the fermentation.

The prepared aszú-berry samples show different amine-compositions proving the quality difference among noble rotted berries. The amines in aszú-berries partly fortify the results of study on biogen amine-concentration of musts, and partly they give reasons for the low amino acid-concentration of aszú-berries. *(Figure 5 and 6).*

In the year of 2002, we extracted different quality aszú-berries with the same base-wines. The chemical parameters of the base wine, and the raw aszú-wines before the fermentation and aszú-wines after the fermentation are shown in *Table 2.*

The examined samples give information about biogen amines. As *Figure 7* and *8* show, before the fermentation, the histamine-concentration was reduced practically into 0, and there was a measurable decrease in the tiramine-quantity too, while the serotonine gave us a slight increase.

We chose by chance a few wine-samples for demonstrating the amine-composition *(Table 3).*

According to the values of *Table 3* and to the other results we can declare that the biogenic amine-concentrations are higher than in the normal wines in spite of the fact that the aszú wine samples were ready for marketing. In general, the histamine concentration remained under the prescribed limit value, while the serotonine was found in a higher quantity.

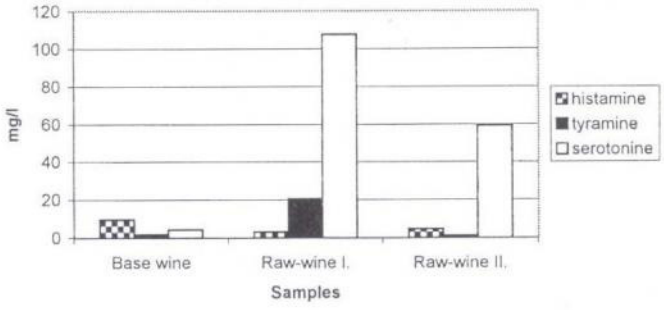

Figure 7 The biogenic amine-composition of aszú steeping experiment before the fermentation

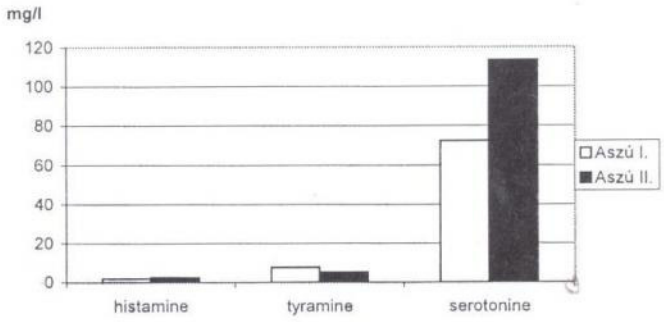

Figure 8 The biogenic amine composition of aszú steeping experiment after the fermentation

Table 2 The chemical composition of raw aszú wines before the fermentation and of aszú wines after the fermentation

	Base wine for steeping	I.		II.	
		Before fermentation	After fermentation	Before fermentation	After fermentation
Sugar (g/l)	38.0	149.0	92.9	143.7	67.7
Alcohol (v/v%)	12.88	10.21	11.40	9.94	13.92
Volatile-acid (g/l)	0.26	0.55	0.57	0.48	0.6
Total polyphenol (mg/l)	176	376	442	412	486
Catechin (mg/l)	31	120	113	132	136
Leucoanthocyanine (mg/l)	87	312	321	417	295
Glycerine (g/l)	10.9	13.86	26.17	13.37	28.07
Gluconic acid (g/l)	0.25	2.29		2.35	
Titrable acid (g/l)	7.3	9.8	9.3	9.9	9.3
pH	3.43	3.45	3.35	3.43	3.29

Table 3 The biogenic amine composition of Tokaji Aszú wines

Samples	Ethylamine	Methyl-amine	Histamine	Tiramine	Serotonine	Putrescine	ßphenyl-ethylamine	Cadaverine	Total biogenic amine
	(mg/l)								
1.	0	0	0	11.75	18.14	21.81	22.42	21.89	96.01
2.	0	0	5.19	7.73	82.73	20.9	22.09	31.11	169.75
3.	0	0	5.79	5.09	86.48	19.76	19.96	28.00	165.08
4.	0	0	5.01	10.69	89.92	18.55	19.95	21.45	165.57
5.	0	0	2.81	4.58	112.76	17.66	19.8	21.87	179.48
6.	0	0	9.8	4.52	15.11	21.3	17.97	20.06	88.76
7.	0	0	3.45	0	0	21.1	17.74	19.56	61.85
8.	0	0	13.41	13.29	0	95.6	35.5	22.96	180.76
9.	0	0	6.44	5.13	21.33	24.03	18.82	22.18	97.93

Conclusions

In our work we have studied the biogenic amine-composition of Tokaji Furmint musts from 2002, that of aszú-berry extracts, raw aszú wines and different aszú wines. The histamine-, tiramine- and serotonine-concentration were measured.

In the case of musts, during the fermentation at the beginning phase there was a decreasing trend in the biogenic amine concentration while in the end of the fermentation an increase was noticed.

The aszú-berry extracts show different biogenic amine-composition.

In the case of aszú-wines consequently the histamine concentration could be measured under the end values, while the serotonine-content was significantly higher.

In the future, the study on the biogenic amine-composition of the Tokaj Wine Specialities will be an indispensable task because the presence of biogenic amines can be regarded as a signal compound for the activity of *Botrytis cinerea* and the noble rotting process.

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