ASPECTS REGARDING THE EVOLUTION OF ACIDITY DURING ALCOHOLIC FERMENTATION OF CERTAIN MUSTS

ASPECTE REFERITOARE LA EVOLUȚIA ACIDITĂȚII ÎN TIMPUL FERMENTAȚIEI ALCOOLICE A UNOR MUSTURI

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Abstract: *These work presents data regarding the acidity variation during the alcoholic fermentation of the must in comparison with the evolution of the main compositional characteristics, respectively, reducing sugars, alcohol, potassium, calcium, sodium cations, and total polyphenols index (ITP). The experiments were conducted on two musts from white varieties (Muscat Ottonel, Fetească albă) and must obtained from a red variety (Cabernet Sauvignon) from Bujoru wine center. Depending on the main acids (tartaric, malic, lactic, succinic, citric and the volatile acids), in all grape musts, during the metabolism of sugars in the wort, there is, generally, an increase in total acidity (to around 7-8 % vol. alcohol), after which it slowly decreases until the end of alcoholic fermentation.*
Key words: *must, acidity, alcoholic fermentation, acids, total polyphenols index.*

Rezumat: *În lucrare se prezintă date referitoare la evoluția acidității în timpul fermentației alcoolice a unor musturi în comparație cu evoluția principalelor caracteristici de compoziție, respectiv zaharuri reducătoare, alcool, cationii de potasiu, calciu, sodiu şi indicile de polifenoli totali (IPT). Experimentările au fost efectuate pe două musturi provenite din soiuri albe (Muscat Ottonel, Fetească albă) şi pe mustuiala obținută dintr-un soi roşu (Cabernet Sauvignon), provenite din centrului viticol Bujoru. În funcție de principalii acizi (tartric, malic, lactic, succinic, citric şi de cei volatili), la toate soiurile, în timpul metabolizării zaharurilor din must, se observă, în general, o creştere a valorii acidității totale (până în jurul valorii de 7-8 % vol. alcool), după care aceasta scade lent până la sfârşitul fermentației alcoolice.*
Cuvinte cheie: *must, aciditate, fermentație alcoolică, acizi, polifenoli totali.*

INTRODUCTION

Knowing the wine acidity composition is very important for oenology, because it permits to correlate the real acidity of wine with the intensity of sower taste, sensed at the sensorial analyses. At gustatory appreciation of the wines acidity, it must take into consideration the fact that the sower taste is influenced also by other compounds as alcohol, glycerol, sugars and by the neutralizing

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effect of potassium and calcium ions (Cotea, 1985). Because of this reason it is necessary that during the alcoholic fermentation, in direct relation with the evolution of the compounds responsible for the acidity, to monitor the formation and modification of the aforesaid compounds. This work presents data regarding the acidity variation (volatile, total and real acidity) during the alcoholic fermentation of the grape must in comparison with the evolution of the principal compositional characteristics, as it is the reducing sugars, alcohol, tartaric, malic, lactic, succinic and citric acids, potassium, calcium and sodium cations and total polyphenols index (IPT).

MATERIAL AND METHOD

The studies regarding the acidity variation during the alcoholic fermentation of grape must were done from September to November 2014, in the wine cellar of SC Eurofruct SRL. The experiments were performed on two grape musts from white varieties (Fetească albă, Muscat Ottonel) and on the marc of one red grape variety (Cabernet Sauvignon), from Bujoru wine center, Dealu Bujorului vineyard. The grapes from the studied varieties were harvested between September 29th and October 17th as follows: Fetească albă on 29th of September, Muscat Ottonel on 4th of October and Cabernet Sauvignon on 17th of October. After crushing and destemming each white grape varieties, by treating it with pectolytic enzymes, macerating it for 24 hours and pressing the marc, were obtained 800 L of grape must from each variety. The grape must was transferred in 900 L stainless steel containers and inoculated with selected yeast strains. The alcoholic fermentation was conducted at control temperature (between 16 and 20 ºC) and ended after 216 hours in case of Muscat Ottonel grape must and 192 hours in case of Fetească albă must. At the initial moment and at different time intervals, respectively at 0, 24, 48, 72, 120, 168 and 216 hours, for Muscat Ottonel variety were taken the samples MO_0, MO_1, MO_2, MO_3, MO_4, MO_5 and MO_6. For Fetească albă at the initial moment and at different time intervals, respectively 0, 24, 48, 72, 96, 120, 168 and 216 hours, were taken the samples FA_0, FA_1, FA_2, FA_3, FA_4, FA_5 and FA_6. The marc obtained by crushing-destemming 1100 Kg red grapes, after treating it with pectolytic enzymes and selected yeast strains, was transferred to a 1300 L stainless steel tanks, with lid, in a room at 20 ± 3ºC. The maceration-fermentation of Cabernet Sauvignon marc took place for 144 hours, after which the must obtained without and with pressing was deposited into an 900 L stainless steel container with a hinged lid and pressure and temperature (16 – 20 ºC) system control. At the initial moment and at different time intervals, respectively at 0, 48, 96, 144, 192, 240 and 600, were taken the samples CS_0, CS_1, CS_2, CS_3, CS_4, CS_5 and CS_6.

Each taken sample, after filtration and decarbonization, was analysed in terms of principal physico chemical analyses. The analyses regarding the principal compositional characteristics (reducing sugars, alcohol, total acidity, volatile acidity, pH, tartric acid, malic acid, lactic acid, succinic acid, citric acid, potassium, calcium, sodium and total polyphenol index – IPT at 280 nm) were done using the methods indicated in national and international standards in force (***2012) or in the scientific literature (Țârdea, 2007; Cotea *et al*. 2009). Together with the absolute values obtained are presented the relative deviations (δr) in (%), which changed the main components of the sample of must analyzed.

The calculation of the concentration of each acid in the must analysed samples was done according to the scientific literature (Ribereau-Gayon *et. al.* 1972; Würdig and Woller, 1989; Odăgeriu *et. al.,* 2005) based on the calculation methodology presented by Odăgeriu, 2006.

RESULTS AND DISCUSSIONS

Tables 1, 2 and 3 present data concerning the evolution of the main compositional characteristics of the must-wine mixture during the alcoholic fermentation at the grape varieties studied. They had, for the most part, similar evolution at the must studied samples.

Thus, the transformation of the initial musts ($FA_{0,}$ MO_0 CS_0) into final wines ($FA_{6,}$ MO_6 CS_6) is shown by the variation of the flowing parameters: 198÷2 g/L reducing sugars, 0.00÷11.55 % vol. alcohol; 4.77÷5.58 g/L $C_4H_6O_6$ total acidity, 0.00÷0.34 g/L $C_2H_4O_2$ volatile acidity; 3.884÷3.874 pH; 3.80÷1.62 g/L total tartaric acid, 0.00÷0.54 g/L succinic acid; 0.00÷0.38 g/L lactic acid; 0.00÷0.18 g/L citric acid; 0.00÷0.32 g/L other acids; 1160÷640 mg/L potassium; 98÷70 mg/L calcium, 19 mg/L sodium, 6.8÷6.0 IPT for Fetească albă; 210÷2 g/L reducing sugars, 0.00÷12.24 % vol. alcohol; 3.48÷5.02 g/L $C_4H_6O_6$ total acidity; 0.00÷0.40 g/L $C_2H_4O_2$ volatile acidity; 4.005÷3.923 pH; 3.33÷1.52 g/L total tartaric acid; 0.00÷0.57 g/L succinic acid; 0.00÷0.43 g/L lactic acid; 0.00÷0.20 g/L citric acid; 0.00÷0.41 g/L other acids; 1200÷790 mg/L potassium; 106÷77 mg/L calcium, 21 mg/L sodium, 8.9÷8.1 IPT for Muscat Ottonel; 227÷4 g/L reducing sugars, 0.00÷13.10 % vol. alcohol; 4.30÷6.35 g/L $C_4H_6O_6$ total acidity; 0.00÷0.75 g/L $C_2H_4O_2$ volatile acidity; 3.495÷3.725 pH; 3.65÷1.37 g/L total tartaric acid; 2.39÷1.02 g/L malic acid; 0.00÷0.72 g/L succinic acid; 0.00÷1.08 g/L lactic acid; 0.00÷0.29 g/L citric acid; 0.00÷0.51 g/L other acids; 1340÷800 mg/L potassium; 114÷88 mg/L calcium, 23 mg/L sodium, 14.6÷44.6 IPT for Cabernet Sauvignon.

Total acidity, expressed as g/L $C_4H_6O_6$, comparing with the initial values in grape musts, at all the studied varieties, raised in proportion of 17.0 % for Feteasca albă, 44.3 % for Muscat Ottonel and 47.7 for Cabernet Sauvignon.

The volatile acidity, expressed as g/L $C_2H_4O_2$, had un increasing trend at all the studied varieties, reaching at the end the value of 0.34 g/L at Fetească albă, 0,40 at Muscat Ottonel and 0.75 at Cabernet Sauvignon.

Total tartaric acid (H_2T) concentration linearly decreases at all the studied samples, respectively in percentages of 57,4 at Fetească albă, 54.4 at Muscat Ottonel and 62.5 at Cabernet Sauvignon. Malic acid (H_2M) registered constant values of 2.12 and 1.45 g/L at Fetească albă and Muscat Ottonel varieties and decreases in percentage of 43.9 at Cabernet Sauvignon variety, as a result of partial malolactic fermentation that took place simultaneous with the alcoholic fermentation.

Table 1

Variation of main compositional characteristics of Fetească albă musts during alcohol fermentation

Sample	Time (hours)	Total sugars		Alcohol		Total acidity		Volatile acidity		Real acidity (pH)		Total tartaric acid (H_2T)		Malic acid (H_2M)	H_2T/ H_2M ratio
		g/L	o_r (%)	% vol.	δ_r (%)	g/L $C_4H_6O_6$	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	
FA_0	0	198	0.0	0.00	0.0	4.77	0.0	0.00	0.0	3.884	0.0	3.80	0.0	2.12	1.79
FA_1	24	158	-20.2	2.34	20.3	5.34	11.9	0.02	5.9	3.770	-2.9	3.52	-7.4	2.12	1.66
FA_2	48	99	-50.0	5.85	50.6	6.04	26.6	0.10	29.4	3.642	-6.2	3.35	-1.,8	2.12	1.58
FA_3	72	65	-67.2	7.84	67.9	6.36	33.3	0.16	47.1	3.511	-9.6	3.07	-19.2	2.12	1.45
FA_4	120	32	-83.8	9.76	84.5	5.75	20.5	0.22	64.7	3.662	-5.7	2.22	-41.6	2.12	1.05
FA_5	168	13	-93.4	10.88	94.2	5.68	19.1	0.27	79.4	3.755	-3.3	1.95	-48.7	2.12	0.92
FA_6	216	2	-99.0	11.55	100.0	5.58	17.0	0.34	100.0	3.874	-0.3	1.62	-57.4	2.12	0.76

Table 1 (continued)

Sample	Time (hours)	Succinic acid		Lactic acid		Citric acid		Other acids		Potassium (K^+)		Calcium (Ca^{2+})		Sodium (Na^+)	IPT
		g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	mg/L	δ_r (%)	mg/L	δ_r (%)	mg/L	D_{280}
FA_0	0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.00	1160	0.0	98	0.0	19	6.8
FA_1	24	0.17	31.5	0.05	13.2	0.03	16.7	0.07	1.19	1090	-6.0	97	-1.0	19	6.7
FA_2	48	0.31	57.4	0.13	34.2	0.06	33.3	0.19	3.22	1060	-8.6	89	-9.2	19	6.5
FA_3	72	0.40	74.1	0.20	52.6	0.10	55.6	0.24	4.07	1005	-13.4	82	-16.3	19	6.4
FA_4	120	0.46	85.2	0.27	71.1	0.12	66.7	0.26	4.40	800	-31.0	73	-25.5	19	6.3
FA_5	168	0.49	90.7	0.33	86.8	0.14	77.8	0.29	4.91	730	-37.1	71	-27.6	19	6.2
FA_6	216	0.54	100.0	0.38	100.0	0.18	100.0	0.32	5.42	640	-44.8	70	-28.6	19	6.0

Table 2

Variation of main compositional characteristics of Muscat Ottonel musts during alcohol fermentation

Sample	Time (hours)	Total sugars		Alcohol		Total acidity		Volatile acidity		Real acidity (pH)		Total tartaric acid (H_2T)		Malic acid (H_2M)	H_2T/H_2M ratio
		g/L	δ_r (%)	% vol.	δ_r (%)	g/L $C_4H_6O_6$	δ_r (%)		δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	
MO_0	0	210	0.0	0.00	0.0	3.48	0.0	0.00	0.0	4.005	0.0	3.33	0.0	1.45	2.30
MO_1	24	160	-23.8	2.92	23.9	4.10	17.8	0.05	12.5	3.893	-2.8	2.98	-10.5	1.45	2.06
MO_2	48	104	-50.5	6.24	51.0	4.78	37.4	0.14	35.0	3.842	-4.1	2.56	-23.1	1.45	1.77
MO_3	72	73	-65.2	8.05	65.8	5.00	43.7	0.22	55.0	3.812	-4.8	2.38	-28.5	1.45	1.64
MO_4	120	33	-84.3	10.43	85.2	5.09	46.3	0.27	67.5	3.835	-4.2	2.17	-34.8	1.45	1.50
MO_5	168	12	-94.3	11.64	95.1	5.05	45.1	0.33	82.5	3.886	-3.0	1.87	-43.8	1.45	1.29
MO_6	216	2	-99.0	12.24	100.0	5.02	44.3	0.40	100.0	3.923	-2.0	1.52	-54.4	1.45	1.05

Table 2 (continued)

Sample	Time (hours)	Succinic acid		Lactic acid		Citric acid		Other acids		Potassium (K^+)		Calcium (Ca^{2+})		Sodium (Na^+)	IPT
		g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	mg/L	δ_r (%)	mg/L	δ_r (%)	mg/L	D_{280}
MO_0	0	0.00	0.0	0.00	0.0	0.00	0.0	0.00	0.00	1200	0.0	106	0.0	21	8.9
MO_1	24	0.20	35.1	0.10	23.3	0.05	25.0	0.04	0.68	1120	-6.7	102	-3.8	21	8.8
MO_2	48	0.34	59.6	0.18	41.9	0.08	40.0	0.28	4.74	1025	-14.6	95	-10.4	21	8.6
MO_3	72	0.43	75.4	0.25	58.1	0.12	60.0	0.33	5.59	985	-17.9	88	-17.0	21	8.5
MO_4	120	0.49	86.0	0.32	74,.4	0.14	70.0	0.35	5.93	950	-20.8	81	-23.6	21	8.4
MO_5	168	0.52	91.2	0.38	88.4	0.16	80.0	0.38	6.44	870	-27.5	79	-25.5	21	8.3
MO_6	216	0.57	100.0	0.43	100.0	0.20	100.0	0.41	6.94	790	-34.2	77	-27.4	21	8.1

Table 3

Variation of main compositional characteristics of Cabernet Sauvignon musts during alcohol fermentation

Sample	Time (hours)	Total sugars		Alcohol		Total acidity		Volatile acidity		Real acidity (pH)		Total tartaric acid (H_2T)		Malic acid (H_2M)		H_2T/ H_2M ratio
		g/L	δ_r (%)	% vol.	δ_r (%)	g/L $C_4H_6O_6$	δ_r (%)		δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	
CS_0	0	227	0,0	0.00	0.0	4.30	0.0	0.00	0.0	3.495	0.0	3.65	0.0	2.39	0.0	1.53
CS_1	48	167	-26.4	3.52	26.9	4.86	13.0	0.33	44.0	3.428	-1.9	2.67	-26.8	2.32	-2.9	1.15
CS_2	96	129	-43.2	5.76	44.0	5.45	26.7	0.41	54.7	3.487	-0.2	2.25	-38.4	2.24	-6.3	1.00
CS_3	144	97	-57.3	7.65	58.4	6.68	55.3	0.57	76.0	3.524	0.8	2.05	-43.8	1.78	-25.5	1.15
CS_4	192	61	-73.1	9.78	74.7	6.64	54.4	0.63	84.0	3.602	3.1	1.90	-47.9	1.56	-34.7	1.22
CS_5	240	28	-87.7	11.72	89.5	6.51	51.4	0.68	90.7	3.668	4.9	1.75	-52.1	1.45	-39.3	1.21
CS_6	600	4	-98.2	13.10	100.0	6.35	47.7	0.75	100.0	3.725	6.6	1.37	-62.5	1.34	-43.9	1.02

Table 3 (continued)

Sample	Time (hours)	Succinic acid		Lactic acid		Citric acid		Other acids		Potassium (K^+)		Calcium (Ca^{2+})		Sodium (Na^+)	IPT
		g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	g/L	δ_r (%)	mg/L	δ_r (%)	mg/L	δ_r (%)	mg/L	D_{280}
CS_0	0	0.00	0.0	0.00	0,0	0.00	0.0	0.00	0.0	1340	0.0	114	0.0	23	14.6
CS_1	48	0.24	33.3	0.29	26,9	0.13	44.8	0.16	31.4	1090	-18.7	112	-1.8	23	23.4
CS_2	96	0.48	66.7	0.45	41,7	0.16	55.2	0.20	39.2	990	-26.1	107	-6.1	23	297
CS_3	144	0.65	90.3	0.83	76,9	0.21	72.4	0.33	64.7	960	-28.4	98	-14.0	23	36.6
CS_4	192	0.67	93.1	0.94	87,0	0.23	79,3	0.45	88.2	930	-30.6	90	-21.1	23	45.2
CS_5	240	0.68	94.4	1.02	94,4	0.24	82.8	0.48	94.1	890	-33.6	89	-21.9	23	45.0
CS_6	600	0.72	100.0	1.08	100,0	0.29	100.0	0.51	100.0	800	-40.3	88	-22.8	23	44.6

Real acidity or pH had an evolution as follows: at the Fetească albă and Muscat Ottonel samples decreases with 9.6 respectively 4.8% in the first 72 hours, followed by a slightly increasing by the end of fermentation; at the Cabernet Sauvignon samples, decreases with 1.9 % in the first 24 hours (samples CS_0 and CS_1) after which it raises with 6.6 % at the end (sample CS_6).

Data about the evolution of the acids originating from the initial grape musts and those formed during the alcoholic fermentation at the studied samples are presented in table 4.

Table 4

Acids content variation (% meq/L) originating in must ant of those formed during alcoholic fermentation (A.F.) for studied varieties

No.	Sample	Time (hours)	Must acids	Acids from (A.F.)
Fetească albă				
1.	**FA_0**	0	100.00	0.00
2.	**FA_1**	24	93.53	6.47
3.	**FA_2**	48	85.90	14.10
4.	**FA_3**	72	80.75	19.25
5.	**FA_4**	120	74.70	25.30
6.	**FA_5**	168	70.97	29.03
7.	**FA_6**	216	66.12	33.88
Muscat Ottonel				
1.	**MO_0**	0	100.00	0.00
2.	**MO_1**	24	90.03	9.97
3.	**MO_2**	48	77.61	22.39
4.	**MO_3**	72	71.73	28.27
5.	**MO_4**	120	67.38	32.62
6.	**MO_5**	168	62.89	37.11
7.	**MO_6**	216	57.35	42.65
Cabernet Sauvignon				
1.	**CS_0**	0	100.00	0.00
2.	**CS_1**	48	80.02	19.98
3.	**CS_2**	96	71.04	28.96
4.	**CS_3**	144	58.26	41.74
5.	**CS_4**	192	52.77	47.23
6.	**CS_5**	240	49.40	50.60
7.	**CS_6**	600	43.41	56.59

As it can be seen in table 4, for the studied varieties (Fetească albă, Muscat Ottonel, Cabernet Sauvignon) the percentage value of the acids that originate from must (tartaric, malic) expressed as meq/L, decreases at 66.12, 57.35 and 43.41% and those formed during the alcoholic fermentation (succinic, lactic, citric, volatile, other acids) increases to 33.88, 42.65 respectively 56.59%. it can be seen that from one grape variety to another, directly proportional with the increase of sugar content registered at harvest, increases the content of the acids formed during the alcoholic fermentation.

The variation of the acids at the studied varieties, presented in table 4, suggests the identification of technological methods to preserve the acids at the grape level and especially during the alcoholic fermentation when biochemical imbalances occur.

CONCLUSIONS

1. During the sugar metabolism in must, generally, it can be observed that to around 7-8% vol. alcohol there is an increase of total acidity, dependent of the evolution of the acids (tartaric, malic, succinic, citric, lactic and the volatile ones) and the cations (potassium, calcium), after which it slowly decreases until the end of alcoholic fermentation.

2. In direct correlation with the acids and cations above mentioned, the real acidity (pH), at all the fermented must, decreases in the first part of the fermentation, until the alcohol reaches the value of 5-7 % vol., after which it rises to the end of alcoholic fermentation.

3. Knowledge of mutual dependence between acids and cations of must and wine allows assessing the position of the equilibrium of many ionization reactions of acids present that facilitate theoretical understanding of phenomena, occurring during fermentation of musts, relating in particular to the tartaric compounds insolubilization.

4. Data regarding the variation of acids derived from both initial musts and those formed during alcoholic fermentation can be used to optimize the technologies for winemaking.

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