The Influence of Iron on the Colour of Red Wines

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The antochians are the pigments responsible of the color of the young red wine[7]. Among the antochians, the malvidine has the most important role in the coloring of the red wines. On its stability depends to a great extent the colouring tint and the sensorial particularities of the red and rose wines coming from various vineyards [8]. In the presence of the oxygen and of the iron, the malvidine suffers a degradation process, determining the depreciation of the wines [1; 3; 5]. In this paper was studied the malvidine-3-glucoside degradation kinetic, in model solutions of synthetic wine, in the presence of different concentrations of iron, at 70° C and two values of pH characteristic for the wines (2.9 and 3.4).

Keyword: malvidine-3-glucoside, iron, catalytic effect

The malvidine is an antochian with low hydrophilic character due to the two methoxy groups located on the aromatic ring. These stabilize the aromatic chain and cancel its behaviour of poly phenol with vicinal OH functions (fig. 1).

In grapes and other vegetal sources, the malvidine appears under hydrolysable mono and di-O-glycoside according to the reactions from figure 1.

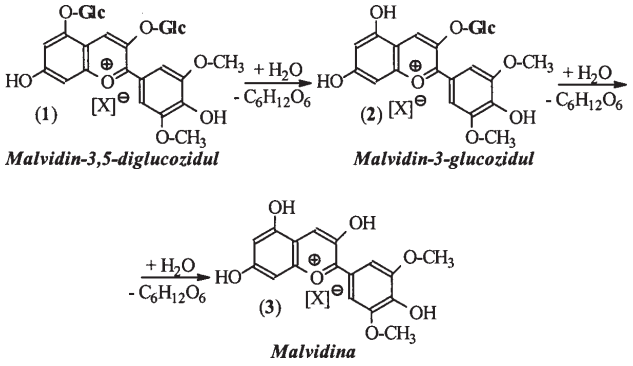

Fig. 1. Maldivin and his glucosides

In the wines of "*Vitis vinifera*" category, the concentration of antochians varies between 350 and 1500 mg/L. These wines contain only 3-O-monoglycoside. Among the antochians, the malvidine-3-O-glucoside represents from 50% in Sangiovese categories up to 90% in Grenache-tinctorial categories [2; 4; 6].

During the period of the preservation of plants reached in polyphenols and food products obtained from their manufacturing were observed progressive changes in taste, colour and colloidal stability. The explications towards these complicated processes based on the results coming from the model systems, at the *p*H of the natural system.

Experimental part

From the malvidine-3-glucoside powder of a 90% purity was prepared a stock solution of malvidine-3-glucoside of 300 mg/L (0.6 mmoles/L) using as solvent a solution of synthetic wine that contains 12% ethanol (Carlo Erba, Italy), 5g/L tartaric acid (Merck), water of chromatographic purity – Milli Q (Milipore, USA) and the pH used was of 2.9 respectively 3.4 (adjusted with NaOH 1 n solution).

These stock solutions of malvidine-3-glucoside 300 mg/L of *p*H 2.9 and 3.4 were used for studying the degradation of this majority antochian from the wines in the presence of different concentrations of iron, at temperature 70°C for 24 h.

From the stock solution of malvidine-3-glucoside were prepared work solutions of 150 mg/L, by dilutions corresponding to the solution of synthetic wine.

In these work solutions were added solutions of known iron concentrations, prepared also from iron sulphate (Labosi, Fisher Scientific, France) in synthetic wine solution.

The concentrations in iron of the used solutions were verified through the method of spectrophotometry of atomic absorption, modern method that allows the determination of the total iron from the solution. The device that was used for this determination was Perkin - Elmer 100, with nitrogen-acetylene oxide flame.

The calibration of the device performed with Milli Q water (Millipore) as blank and for the determination of the iron was used the wavelength 248.3 nm, and the used lamp was multi-element.

The malvidine-3-glycoside degradation was monitored using liquid chromatography at high pressure (HPLC).

The solution obtained in this way was injected in a device HPLC Varian, provided with diodes barriers in the following work conditions:

Device: Varian System, Pro Star 210/215, USA

Debit: 1 mL/min, temperature: ambient

Injected volume: 20µL rendered soluble in mobile phase A

Column: Beckman ODS ultra spheres (250*4.6mm, 5µm) provided with a pre-column from the same phase, detector: 280 and 520 nm

Mobile phase:

Solvent A: water/formic acid (90/10v/v)

Solvent B: methanol / formic acid (90/10v/v)

Elution gradient:

Time(minutes)	0	3	18	28	43	63	64	68	69
% solvent B	2	2	10	20	30	70	100	100	2

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Table 1

pH	Concentration of iron	Equations	k(h^{-1})	r^2	$t_{1/2}$(h)
2.9	Witness with oxygen	Y=-0.0414x-0.0069	0,0414	0,9935	16,7
	Witness without oxygen	Y=-0,0343 x	0,0343	0,99	20,2
	The sample with 0.56 mg/L Fe	Y=-0.0536x-0.0849	0.0536	0.9886	12.9
	The sample with cu 5.6 mg/L Fe	Y=-0.0795x+0.0956	0.0795	0.9901	8.7
	The sample with 11.2 mg/L Fe	Y=-0.0809x+0.1023	0.0809	0.9504	8.5
	The sample with 22.4 mg/L Fe	Y=-0.0838x+0.1458	0.0838	0.972	8.2
3.4	Witness with oxygen	Y=-0.0336x-0.006	0.0336	0,9908	21,5
	The sample with 0.56 mg/L Fe	Y=-0.0376x-0.006	0.0376	0.995	18,4
	The sample with cu 5.6 mg/L Fe	Y=-0.0572x-0.004	0.0572	0.9992	12,1
	The sample with 11.2 mg/L Fe	Y=-0.0594x-0.0494	0.0594	0.9964	11,7
	The sample with 22.4 mg/L Fe	Y=-0.0629x+0.025	0.0629	0.9985	11

For the study of the degradation reactions were prepared test samples of 2 mL where were added the volumes of malvidine-3-glucoside solution and the appropriate iron solutions.

In parallel with the solutions containing iron were prepared also witness tests, some witness tests being prepared in the presence of the oxygen from air and others under nitrogen atmosphere.

Results and discussions

In the actual study was supervised the kinetic of the degradation product of malvidine-3-glucoside in the presence of iron ions at different temperature and of *p*H values.

The constants of apparent speed (k) were calculated by the kinetic model of order one by the help of the following equation:

$$\ln (C_t/C_0) = -k \cdot t \quad (1)$$

where:

C_0 = first concentration în malvidin-3-glucozid

C_t = concentration malvidin-3-glucozid at time of reaction t

The half-time of reaction ($t_{1/2}$) is given by equation :

$$t_{1/2} = \ln(0,5)/k \quad (2)$$

The regression equations obtained for malvidin-3-glucoside degradation in the iron presence and the values of kinetic parameters coresponding to the temperature of 70°C, for 24 h period at two values of the *p*H are presented in table 1.

In figure 2 is presented the variation of the rate constants of the malvidine-3-glucoside degradation process at the temperature of 70°C and *p*H = 2.9 in the presence of different iron concentrations.

By analyzing the influence of the iron over the malvidine-3-glucoside degradation process, result the following observations:

-the iron has a catalytic effect towards the malvidine-3-glucoside degradation; the half-time is smaller in compared with the time corresponding to reference, tests in the same temperature conditions;

-the catalytic effect of the iron is proportional with the iron quantity from the solution; at concentrations higher than 0.1 mmoles/L iron, the catalytic effect is less shown;

-given the situation of the reference test of which half-time is of 16.7 h , the test that contains 0.56 mg/L Fe(II) has a half-time of 12.9 h, meaning a decreasing of 22.75%,

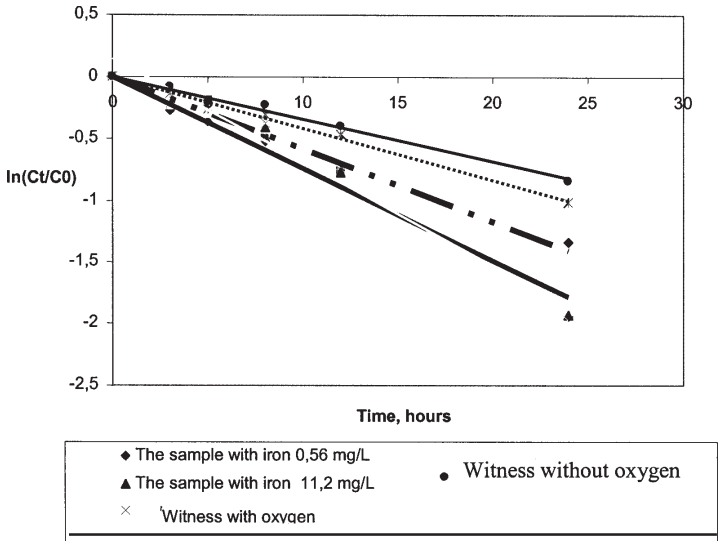

Fig. 2. The variation of the rate constants of malvidine-3-glucoside degradation process at the temperature of 70°C and *p*H = 2.9 in the presence of several iron concentrations

while a ten time increasing of the iron quantity (test 2 with 5.6 mg/L iron) determines a half-time decreasing of 47.9% in comparision with the reference test and only 25.15% in respect with the previous test;

-when the iron concentration is two times bigger, the half-time of test 3 decreases only 2.3% in comparison with the previous test;

-at the *p*H of the solution of 3.4 the catalytic effect of the iron decreases; by the increasing with 10 times the iron concentration, the half-time is diminished about 34.2%.

Conclusions

The study regarding the kinetic of the catalytic degradation of malvidine-3-glucoside from the red wines, leads to the following conclusions:

- the iron has catalytic effect at the temperature of 70°C both at *p*H 2.9 and *p*H 3.4;
- the malvidine-3-glucoside degradation is proportional with the iron concentration from the solution;
- at the same temperature and at the same time period, the malvidine-3-glucoside degradation is more pronounced at lower *p*H values.

References

1.ALECU A,, SAUCIER C., CREŢESCU I., 2008, Rev. Chim. (Bucureşti), **59**, nr. 3, 2008, p. 314
2. FRANCIS F.J., 1989, Anthocyanins. Crit. Rev. Food Sci. Nutr., 28 , p. 273
3. FURTADO P., FIGUEIREDO P., PINA F., 1993, Photochemical and thermal degradation of anthocyanidins- Journal Photochemistry Photobiology, 75, p.113
4. GLORIES Y., 1984, La couleur des vins rouges- Connaissance vigne vin, 18, p.1165
5. LOPEZ P., 2005, L' etude des phenomenes oxydatifs pendant le vieillissement des vins. Role de l'obturateur, Thèse de doctorat, Bordeaux, France
6.MAZZA G., MINIATI E, 1993, Anthocyanins in Fruits, Vegetables and Grains, CRC Press, London
7.RIBEREAU-GAYON P., GLORIES Y., DUBOURDIEU D, 1998, Les composes phenoliques-Tratait d'Oenologie, Tome 2-Chimie du vin.Stabilisation et traitements, Dunod, Ed.Paris
8.ŢÂRDEA C., SÂRBU GH., ŢÂRDEA A., 2000 , Tratat de vinificaţie- Editura Ion Ionescu de la Brad, Iaşi

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