The Study of Catalytic Degradation of Malvidin-3-Glucoside from Red Wines, using Molecular Absorption Spectrophotometry

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The presence of oxygen and heavy metals naturally found in red wines, leads to the depreciation of their qualities, due to the malvidin-3-glucoside degradation. In this paper, the kinetic of the malvidin-3-glucoside degradation, in synthetic wine model solutions, in the presence of different concentrations of iron and copper, at a temperature of 70°C and two pH values of the wines (2.9 and 3.4 respectively), was studied using the molecular absorption spectrophotometry method.

Keywords: malvidin-3-glucoside, wine qualities degradation, iron, copper

Anthocyanins are the pigments responsible for the color of the young red wine, having usually a concentration in wine, between 350 mg/L up to 1500 mg/L [1, 2]. The color of these pigments depends on their chemical structure and chemico-physical conditions of the environment: pH, temperature, sulfur dioxide, light, catalytic metals [3]. The molecules of anthocyanins are not very stable and therefore their concentration in wine decreases in time. This diminution is given on one hand by the combining reactions with different components of wine, for example tannins, and on the other hand is due to the degradation reactions [2; 4].

The anthocyanins could be transformed into the following compounds, depending on the experimental conditions of degradation process:
- calcinone, in alkaline environment [1];
- malvone, under peroxides action;
- dihydroflavonols, in the presence of the alcohol [5].

Thermal degradation of the anthocyanins takes place according to the reaction scheme presented in figure 1. Depending on the anthocyan type, various products of degradation are obtained, but 2,4,6-trihydroxybenzaldehyde is common for all the anthocyanins that undergo a thermal degradation process because is formed from A cycle. The other formed products depend on the substitutes of the lateral B cycle of anthocyanins. In the malvidin-3-glucoside case, the obtained product is siringic acid.

Oxidative degradation of the anthocyanins

The molecular oxygen cannot react directly with the organic compounds due to its electronic configuration, but in the presence of catalytic metals such as iron and copper, in the solution, oxygen is transformed into peroxides.

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Malvidin-3,5-diglucoside can undergo a nucleophilic attack at C2 of the flavylium cation, stimulating a breaking of the pyrylium cycle leading to esters of o-benzoiloxy-phenyl acetic acid (malvones), through the Bayer-Villiger oxidation [7].

The malvones are easily hydrolyzed in acid media and can lead to siringic acid, glucoside-2,4,6-trihydroxy-phenyl-acetic acid or coumarone, depending on the pH value.

The cascade of the oxidation reactions continues with the formation of 8-β-D-glucopyranosil-2,4-dihydroxy-6-oxociclohexa 2,4-dienyliden acetate. This compound, being a quinonic form, which comes from the degradation of malvidin-3-glucoside, was named malvidone [8].

Experimental part
Two stock-solution of malvidin-3-glucoside of 300 mg/L (0.6 mM/L) were prepared using malvidin-3-glucoside powder (90 % purity), and a solvent solution of synthetic wine that contains 12% ethanol, 5g/L tartaric acid and ultra-pure water provided by Milli Q Water Equipment (Millipore). The former stock-solution had a pH value of 2.9 and the latter 3.4 (adjusted with NaOH 1 N solution).

These 300 mg/L malvidin-3-glucoside stock solutions, with 2.9 and 3.4 respectively pH values, were used afterwards, in order to study the anthocyan degradation in wine, in the presence of iron and copper, at 70°C, for 24 h.

Work solutions of 150 mg/L were prepared from the malvidin-3-glucoside stock solutions.

Iron and copper solutions, with known concentrations, in the synthetic wine were prepared (for iron the concentrations of the solutions were: 0.56, 5.6, 11.2, 22.4 mg/L, and for the copper the concentrations of the solutions were: 0.63, 1.26, 6.3, 10 mg/L).

The malvidin-3-glucoside degradation was studied by the molecular absorption spectrometry, using a UV-VIS spectrophotometer, type Kontron Uvikon 922 (Italy), monitoring the absorption spectra scanned between 250 nm and 700 nm.

According to the literature [9], the degradation products of malvidin-3-glucoside have absorption maxims of 290 nm and 335 nm respectively.

Anthocyanins, usually present an absorption maximum at 520 nm.

A spectral scavenging between 250 nm and 700 nm, for all the studied solutions (the initial solutions, the incubated solutions (70°C), at different pH values, in the presence of iron and copper) was made according to the above mentioned method. Meanwhile, a spectral scavenging of the reference samples was made.

By comparing the absorbance at 290 nm, 335 nm and 520 nm corresponding to the initial samples, containing iron and respectively copper, the final samples, after a certain reaction time, and the reference samples, the catalytic influence of these two metals on the malvidin-3-glucoside color degradation can be observed.

Results and discussions
Iron presents a catalytic effect on the malvidin-3-glucoside degradation explained through the decrease of the absorbance at 520 nm. Thus, at 70°C, the absorbance of the malvidin-3-glucoside solutions decreases proportionally with the increasing of iron concentration in the samples. If there are smaller iron concentrations in the samples (as tests 1; 2 and 3, with iron content between 0.56 mg/L and 11.2 mg/L), the pH plays an important role, meaning that in acid solutions the decreasing of the absorbance is more accentuated, so the degradation effect is stronger.

Oxygen determines a colour degradation of the malvidin-3-glucoside solutions. Thus for reference sample with oxygen, the absorbance at 520 nm is smaller than that of reference sample with low oxygen content, prepared in nitrogen atmosphere. A lower pH value determines a more accentuated color decreasing of the malvidin-3-glucoside solutions (table 2). Also, oxygen presence determines an increasing of the absorbance at 290 nm and 335 nm.

The absorbance at 290 nm for malvidin-3-glucoside containing samples increases proportionally with iron concentration. The absorbance increasing is justified by the issue of new malvidin-3-glucoside degradation compounds, which present a maximum absorption at 290 nm, as it was reported in literature. If lower iron
concentrations of the malvidin-3-glucoside samples (between 0.56 mg/L and 5.6 mg/L) are used, the increasing of the absorbance is more pronounced at a pH value of 2.9. If there's a higher iron concentration (test 4, 22.4 mg/L iron), the variation of the absorbance is almost independent of the pH value.

At 335 nm, the absorbance proportionally increases with iron concentration, for the malvidin-3-glucoside samples. The pH presents a critical influence on the color degradation of the malvidin-3-glucoside solutions.
If higher iron concentrations (22.4 mg/L) are used, the influence of pH is lower. Thus, at a pH value of 2.9 the absorbance increases only 26.7%.

The catalytic effect of copper, at 70°C, is emphasized by the decreasing of the absorbance for malvidin-3-glucoside solutions, measured at 520 nm. For a lower pH value, a more accentuated color degradation of the malvidin-3-glucoside solutions, with lower iron concentrations in the samples (samples with copper content between 0.63 mg/L and 1.26 mg/L) can be observed. At higher copper concentrations (6.3 mg/L) and higher pH values, a more pronounced decreasing of the absorbance at 520 nm occurs.

In the presence of copper, at 70°C, the absorbance of the malvidin-3-glucoside samples, recorded at 290 nm, gets higher with the increasing of copper concentration. The increasing of the absorbance values is accelerated at higher pH values (table 3).

The malvidin-3-glucoside samples that contain copper, at 335 nm, kept at 70°C for 24 h, at a pH value of 3.4, lead to a proportional increasing of the absorbance with the copper concentration.

At a pH value of 2.9, the most powerful catalytic effect was observed for a copper content of 1.26 mg/L. The highest value was recorded at 335 nm.

At higher values of copper concentration in the malvidin-3-glucoside solutions, the absorbance at 335 nm records a decreasing. If more than 1.26 mg/L copper is used, an inhibitory effect on the issuing of the malvidin-3-glucoside degradation products is observed (table 3).

Conclusions

In this paper, a kinetic study of the catalytic degradation of malvidin-3-glucoside from red wines, using the molecular absorption spectrophotometry method was presented, in order to point out the depreciation of the wine quality, due to the heavy metals naturally present in red wines. Among these heavy metals, the iron and copper have a more common presence:

- iron presents a catalytic effect at 70°C, either at a pH of 2.9 or 3.4; due to this effect, iron presence determines a decreasing of the absorbance for the malvidin-3-glucoside solutions at 520 nm, and an increasing of the absorbance at 290 nm and respectively 335 nm (wavelength characteristic to the absorption of the malvidin-3-glucoside degradation compounds), comparing to the reference samples;
- the malvidin-3-glucoside degradation is proportional with iron concentration in solution;
- at similar temperature and degradation periods, the malvidin-3-glucoside degradation is more pronounced at lower pH values;
- iron presents a better catalytic effect than copper, in the same experimental conditions: temperature, time and concentration (expressed in mM/L).

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Manuscript received: 123.11.2007