RESISTANCE TO OXIDATION OF WHITE WINES. RELATIONSHIP BETWEEN POTENTIOMETRIC MEASUREMENTS AND SUBSTANCES RESPONSIBLE FOR AROMA DEGRADATION

A.C. Silva Ferreira, C. Oliveira, T. Hogg and P. Guedes de Pinho

Escola Superior de Biotecnologia, Universidade Católica Portuguesa, Rua Dr. António Bernardino de Almeida, 4200-072, Porto, Portugal

INTRODUCTION

In wine making, the redox phenomena are responsible for profound changes in the wine's chemical composition. The aromatic degradation is largely caused by these redox mechanisms (1) and has been reported, in several works, that occurs prior to the chromatic degradation (2, 3, 4). These alterations make up what is commonly known as "oxidative spoilage" and are dependent of the wine "resistance to oxidation". Various researchers have tried to reproduce in the laboratory, the "aroma degradation" associated with "oxidative spoilage" (2, 5, 6). From an industrial point of view, it should be noted that, there is no systematic way to predict the shelf-life of bottled white wines. The determination of the "resistance to oxidation", done by a developed potentiometric method (7) could be used as a control method. The aim of this work was to relate three parameters:

- the "Index of Degradation" (ID) evaluated by sensorial analysis;
- the "Resistance to Oxidation" (ROX) measured by potentiometric titrations;
- the levels of substances responsible for "off-flavours", in order to give more information concerning "white wine oxidative spoilage" (OSW) as an attempt to predict white wines shelf-life.

MATERIAL AND METHODS

Wine material

- **Wine Group I:** wines coming from a "forced ageing" experiment (6).
- **Wine Group II:** 24 white wines (1-20 years old).
- **Wine Group III:** 35 wines coming from several world regions (3-6 years old), 5 were saturated with O_2 and stored at T = 30ºC (10 days).

Scoring and Similarity testing

Data were treated according to a "scoring test" and statistical significance was evaluated (8). The "Index of Degradation" (ID) was determined by a comparison test of each sample and a white wine considered as "oxidative spoilage".

Potentiometric titration

Using a TITRALAB automatic system with a combined platinum electrode (7) a sequence of redox titrations, reduction/oxidation using $TiCl_3$ and dichlorophenolindophenol was performed. The quotient between the oxidized and reduced fractions (ROX-value) could be related with the "degree of oxidation" of a wine. Hence, ROX-value traduces this status and was obtained by the formula: [(mmol Red)/(mmol Oxi) × 10].

Other quantification methods

Volatile analysis was performed by GC-MS (9) and the concentration of dissolved O_2 was measured using a "WTW 340 Oxygen Probe".

RESULTS AND DISCUSSION

Sensory analysis

The descriptors related to aroma of "OSW" were: "honey-like", "farm-feed", "hay" and "woody-like" (5). Group I and Group II wines were submitted to chemical and sensorial analyses and the coefficients of correlation between sensorial descriptors and ROX are shown in *table I*.

Table I: ***Correlation coefficient between ROX and sensory descriptors and "Index of Degradation"***

Correlation Coefficient (r) with ROX	Wine Group I Forced ageing experiment (n = 13)	Wine Group II Commercial wines (n = 24)
"Index of Degradation" (ID)	0.8356	0.8831
"foral"	– 0.7556	– 0.7884
"honey-like"	0.7452	0.7925
"hay"	0.7145	0.8457
"woody-like"	0.6921	0.8536
"farm-feed"	0.8108	0.8405

High correlation values were obtained between potentiometric measurements and sensorial analysis, in particular for the ID.

Chemical analysis

The molecules described as "key odorants" were: methional (highest impact), phenylacetaldehyde, sotolon and TDN (6). Relationship between ROX, methional and phenylacetaldehyde were first studied on Group I wine samples.

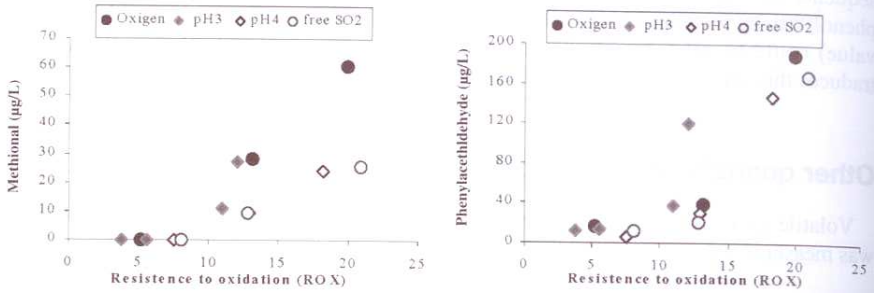

Figure 1: ***ROX in function of [C] in methional and phenylacethaldehyde*** **(group I wines)**

Methional was not detected in samples with ROX-values < 10. Above this value the quantities of methional were above olfactive threshold (LDO = 5 $\mu g \cdot L^{-1}$). The same behaviour was observed for phenylacetahldehyde (LDO = 25 $\mu g \cdot L^{-1}$) (*figure 1*). Finally, TDN and linalool were also correlated with ROX-values, respectively 0.7214 and – 0.8341. Chemical and sensorial analyses of Group II wines are shown in *table II*.

The ranking order based on ROX does not correspond to the respective indicate wine age. Nevertheless, ROX-values were in agreement with ID. Samples containing high levels of methional and phenylacetaldehyde correspond to those with ROX-values close to 10, conversely, linalool concentration was not detected in samples with ROX-values above 10 (*table II* and *figure 2*).

ROX-values measured on Group III ranged from 0.4 to 4.4 and sensorial analysis did not find "aroma spoiled" wines. Five samples, from Group III, were saturated with O_2 and stored at T = 30°C (10 days). The increment between ROX for each sample after oxygen consumption (3.8-4.9 $mg \cdot L^{-1}$) was significant (e.g. 2.5-4.4, ROX).

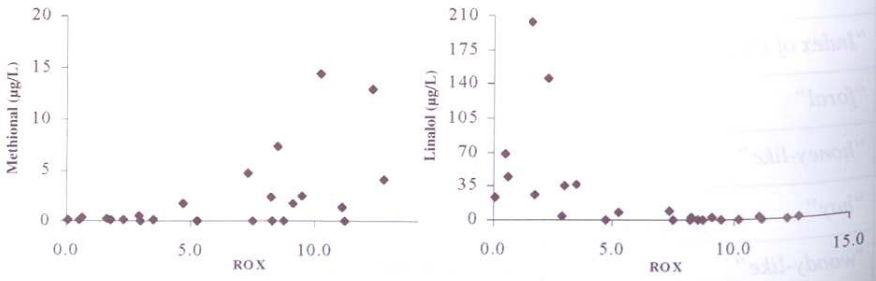

Figure 2: Relationship between methional and linalool concentrations and ROX values (group II wines)

Table II: ***Sensorial and chemical data from commercial wines rankea accoraing ROX***

Samples	*Age*	*ROX*	"Index of Degradation" (ID)	Methional ($\mu g \cdot L^{-1}$)	Phenyla-cetaldehyde ($\mu g \cdot L^{-1}$)	TDN (*area*)	Linalool ($\mu g \cdot L^{-1}$)
DA	18	**13**	17	4.1	5.9	4.2	*n.d.*
TA	9	**12**	15	13.0	16.6	8.2	*n.d.*
TODA	7	**11**	15	0.9	2.8	5.3	*n.d.*
MAS	20	**11**	15	1.4	7.0	3.3	*n.d.*
CCA	17	**10**	17	14.5	33.3	5.6	*n.d.*
CB	14	**9**	17	2.5	6.7	6.8	*n.d.*
CA	17	**9**	16	1.7	4.6	4.0	*n.d.*
TF	4	**9**	12	0.8	3.4	5.9	*n.d.*
DA	7	**8**	12	7.4	10.9	7.0	*n.d.*
CCC	9	**8**	12	*n.d.*	3.9	4.4	*n.d.*
MSB	19	**8**	14	2.4	4.3	4.8	*n.d.*
TE	5	**7**	7	*n.d.*	1.8	4.0	*n.d.*
TB	8	**7**	15	4.7	13.8	9.4	9.2
TD	6	**5**	12	*n. d.*	4.2	8.5	8.5
TC	7	**5**	13	1.7	4.1	6.2	*n.d.*
DVA	10	**3**	9	*n.d.*	0.9	3.2	36.7
DQB	4	**3**	7	*n.d.*	0.9	2.6	35.2
DQA	6	**3**	7	*n.d.*	0.9	4.2	4.2
DVE	3	**2**	2	*n.d.*	*n.d.*	1.6	146.0
DVC	8	**2**	6	*n.d.*	2.9	6.9	27.0
DVD	4	**2**	7	*n.d.*	1.0	3.5	20.4
DVF	2	**1**	4	*n.d.*	3.6	1.2	44.0
DVB	9	**1**	9	*n.d.*	*n.d.*	5.4	68.0
DVG	1	**1**	2	*n.d.*	2.8	0.1	23.0

CONCLUSION

ROX-values were strongly correlated with ID, both in normal aged wines and in samples submitted to a "forced ageing" experiment, respectively r = 0.88 and r = 0.84. ID is better explained by ROX-values than by the indicated wine age. For ROX-values higher than 10, linalool was not detected, and the concentration of methional and phenylacetaldehyde were respectively above 10 $\mu g \cdot L^{-1}$ and 50 $\mu g \cdot L^{-1}$. A relationship was observed between oxygen consumed during the protocol and ROX. Nevertheless more results are needed to validate this last observation. These results could contribute to estimations of the shelf-life for a white wine.

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