TECHNOLOGY AND BIOCHEMISTRY OF WINE

VOLUME 2

JÁN FARKAŠ

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JÁN FARKAŠ
Research Institute for Viticulture and Oenology, Modra, Czechoslovakia

Translated from the Czech by Želimír Procházka

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TECHNOLOGY AND BIOCHEMISTRY OF WINE

Foreword

The *Technology and Biochemistry of Wine* is a comprehensive survey of the science and technology of wine-making. It reflects the extensive experience of the author, derived both from research and from practical work.

An earlier version of this book was published in Czechoslovakia in 1973, and was awarded the 1974 prize of the International Viticultural and Winemaking Organization in Paris and the prize of the Slovak Literary Fund in Bratislava.

This new English translation contains up-to-date technological information concerning the production and treatment of wines. The microbiology, biochemistry and enzymology of wine-making are well covered. Recent advances are covered in the chapter devoted to the biotechnological aspects of the fermentation process. This chapter also contains a discussion of the regulation of the fermentation process and the stages of malo-lactic fermentation.

New physico-chemical methods of identifying turbidity are discussed and the sections on clarification and stabilization are most valuable.

A separate chapter is devoted to the use of wine raw materials for the production of non-alcoholic drinks, distillates, and also the utilization of pomace-cake and yeast sediments. This shows how waste products from wine production can be used, which is important from not only an ecological but also an economic viewpoint.

The chapter "The World of Wine" provides a survey of the types of wine produced in the viticultural areas of the world. This is complemented by informative maps and includes a section on the quality of the wine and its labelling in these areas. The chapters "The Importance of Wine in Human Nutrition" and "Sensory Evaluation and the Quality of Wine" are also very illuminating.

Overall the book gives a comprehensive picture of worldwide wine production.

Professor Farkaš is an outstanding scientist and teacher in the field of wine production, and I believe that this English translation of his book will be greatly welcomed by research workers, and graduate and postgraduate students, as well as all those involved in the wine production process. Experts from the catering and wine trade will find many points of interest, as will consumers.

Professor Dr Rudolph Bretschneider
Czechoslovak Academy of Sciences

Preface

Wine retains its general popularity and reputation due, among other things, to its quality, confirmed at many international exhibitions, and enhanced by technological progress in wine production.

The present book is a contribution to the understanding of the technology and biochemistry of wine. It is a complex work giving answers to many questions which can arise during the production, treatment, evaluation and acquisition of good quality wine.

It contains both general information on viticultural areas of the world and on the types of wine produced in them, concentrating mainly on world famous wines of controlled and acknowledged quality, and on the determination of their quality. It also covers the importance of wine in human nutrition from the point of view of thousands of years of tradition and of new findings concerning the nutritive and hygienic value of wine.

The mainstay of this book are the latest discoveries in the technology, microbiology and biochemistry of wine; the text is based both on my own knowledge, acquired during many years of investigation and practice in this field, and on knowledge from world literature.

The general progress and development of natural sciences, especially microbiology, chemistry and biochemistry, have permitted a better knowledge of the processes taking place during fermentation, formation, maturing and storage of wine, and thus greater possibilities for purposefully intervening in these processes.

Individual chapters of the book link together and give an overall view of the whole of wine production. The basic raw material for the production of wine, i.e. grapes, is analysed primarily. Progressive methods of production of white and red wine are discussed together with recent advances in the microbiology, biochemistry and enzymology of wine and also the processes of controlling fermentation by yeasts, or malic–lactic fermentation. The book gives a survey of new views on the biochemical oxidation–reduction processes taking place at individual stages in the production of wine, i.e. its formation, shaping, maturing and ageing, and it indicates the possibilities of influencing them and of the introduction of new progressive methods for improving the quality of wine.

New knowledge and procedures are also described in the chapter on the identification of turbidities in wine, and in the chapter on the treatment and clarification of wine. Mild methods are stressed, accelerating purification and decelerating maturing and ageing, which mean that bottled wines keep their optimum quality, sparkle and bottle maturity for a longer period than with former methods. At the same time the number of operations is reduced and a considerable economic and ecological improvement is also achieved.

Further chapters are devoted to the production of special, tokay, sparkling and dessert wines. Considerable attention is given to the sensory evaluation and control of wine, prevention of turbidity and the correction of faulty and diseased wines.

The main aim of the book is to ensure production of the best possible wine from given raw materials. I have endeavoured to give an account of the present state of science and research, so that the book deals with the theoretical basis of wine production, as well as discussing the possibilities of solving particular problems, and providing advice for use in practice.

The book will be a great help to research workers and scientists, but also to all those who are involved in the production and treatment of wine, and it will also be a suitable textbook for students, not to mention its service to amateurs and consumers of wine.

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16 The Maturing of Wine

The period of the maturing of wine is characterized by chemical, biochemical and physical changes. These changes influence the formation of taste, bouquet and the general character of the wine.

The most important processes taking place in wine during the maturing period are the degradation of acids by bacteria, the precipitation of tartar and esterification. Oxidation and reduction processes play an important role here.

EFFECT OF OXYGEN ON THE MATURING OF WINE

Solubility of oxygen in wine

Oxidation and reduction processes in wine can be explained in the following manner. Each wine can absorb a certain amount of oxygen. However, the solubility of oxygen in wines varies considerably and, according to Ribéreau-Gayon J. and Peynaud (1966), depends mainly on the wine's temperature and on atmospheric pressure.

If wine is mixed with air at 20 °C, the concentration of oxygen in wine, in ml l^{-1}, is:

after 1 second	2.2
after 2 seconds	3.1
after 5 seconds	4.6
after 10 seconds	5.9
after 30 seconds	5.9

This means that for the saturation of wine with oxygen about 10 seconds are needed, while for the saturation of water 1.5 minutes are required, because ethanol facilitates oxidation. When temperature is decreased the solubility of oxygen in wine increases very much. At 20 °C the wine absorbs

5.6–6 ml l^{-1} of oxygen, at 12 °C, 6.3–6.7 ml l^{-1}: this amount increases to freezing point.

The presence of carbon dioxide decreases the solubility of oxygen in wine. If a young wine containing 100 ml of CO_2 in 1 litre is stirred with an equal amount of air, it absorbs only 3–4 ml of oxygen. Sulphur dioxide also affects the oxidation of wine. It reacts with oxygen, thus preventing the

Table 16.1.

Rate of binding of dissolved oxygen (cm^3 l^{-1}) (Ribéreau-Gayon and Peynaud, 1966)

Temp. (°C)	After 12 hours	After 1 day	After 3 days	After 6 days	After 10 days	After 20 days
30	4.1	5.0	6.0	6.0	6.0	6.0
20	–	2.5	3.7	4.7	5.5	6.0
17	–	1.8	3.1	4.2	5.0	6.0
13	–	1.0	2.0	3.1	4.0	5.2
3	–	–	0.5	1.0	1.7	2.9
2	–	–	0.3	0.6	1.0	2.1

oxidation of other wine components. For the binding of 1 mg of oxygen, 4 mg of SO_2 are needed.

The rate of binding of oxygen by sulphur dioxide depends on temperature. A white wine, sulphurized with 60 mg l^{-1} of sulphur dioxide, was aerated and then stored without access of air at various temperatures. Table 16.1 shows that different amounts of oxygen are bound at different temperatures. The higher the temperature, the more soluble oxygen is bound, and the higher the rate.

Rankine and Pocock (1970) show that the rate of reaction of dissolved oxygen increases with temperature. A red wine saturated with air at 20 °C consumed all the oxygen at this temperature within 14 days, while at 30 °C this took 3 days.

The amount of the dissolved oxygen is expressed in milligrams. Ten milligrams of O_2 in 1 litre correspond to 7 ml l^{-1} or 320 μmol l^{-1} of oxygen. Table 16.2 shows that the amount of the dissolved oxygen depends on the composition of the liquid. Dissolved solids (extract) decrease the ability of the solution to dissolve oxygen, while ethanol increases it. Absorption and binding of oxygen in wine also depends on oxidation of the substances present; this follows from Rodopulo's (1966) survey:

Substrate	Amount of O_2 absorbed in 90 minutes (μmol)
Tartaric acid + Fe^{3+}	0.0
Dihydroxyfumaric acid + Fe^{3+}	205.0
Dihydroxyfumaric acid	135.0
Tartaric acid + Fe^{2+}	125.0
Tartaric acid + dihydroxyfumaric acid + Fe^{2+}	464.0

As is evident from the survey trivalent iron can neither oxidize tartaric acid nor bind oxygen. Tartaric acid can absorb oxygen in the presence of dihydroxyfumaric acid and thus the amount of total absorbed oxygen is greatly increased.

Table 16.2.

Liquid saturated with air at 20 °C (Rankine and Pocock, 1970)

	Distilled water	Wine	Must	NaCl solution (25 %)
Partial pressure (Pa)	20 665	20 665	20 665	20 665
Percentage saturation	100	100	100	100
mg l^{-1}	9.1	7.2	6.5	2*
ml l^{-1}	6.4	5.0	4.6	1.5*

* At 25 °C.

Manipulation of wine under pressure increases the solubility of oxygen distinctly. For example, when wine is drawn with a pump, it can absorb oxygen up to 6 ml l^{-1}. When drawing wine without access of air, using rubber tubes or under CO_2 pressure, the oxygen content increases only little, by about 1 ml l^{-1}. Filtration also increases the amount of oxygen in wine. The degree of oxidation depends on the construction of the filters and the method of filtration. The extent of oxidation is also dependent on polyphenols, which react with dissolved oxygen and limit further oxidation. There are many other substances which have an oxidizing ability. The salts of iron and copper accelerate oxidation.

Oxidation of wine during storage

The volume of wine in barrels decreases during storage. This is due to the escape of carbon dioxide, evaporation and change of temperature. These losses differ in different wines, depending on circumstances. When the volume of wine in barrels decreases, the pressure is reduced so that air can penetrate into it through the cork or pores in the barrel. Thus the wine comes into direct contact with air.

Evaporation is greatly affected by the material from which the barrels are made. In concrete cisterns and tanks the losses are very low, from 0.1 to 1 % per year. In wooden barrels evaporation is stronger, 1.5 to 3.5 % per year, or even more – in young wines often up to 5 %.

The amount of liquid evaporated from wooden barrels depends on many factors, in the first place the size of the barrel. In large barrels evaporation is weaker. The smaller the barrel the larger its surface to volume ratio, which automatically facilitates the access of air. The evaporation of wine is also affected by the age of the barrel, the strength of its walls and finally the chemical composition and age of the wine.

Losses of wine	1st year	2nd year	3rd year
During fermentation	3–4 %	–	–
During evaporation	1–2 %	1–2 %	1–2 %
During manipulation	1–2 %	0.5–1 %	–

The losses observed during the storage of wine are dependent on the temperature and humidity of the cellar. In good cellars evaporation is 1–2 %, while in unsuitable cellars it amounts to 8 % or even more. According to Ribéreau-Gayon. J. and Peynaud (1966) wine evaporates in wooden barrels predominantly through the pores, but aeration also takes place through the free surface, because of evaporation of the wine. As an example, when wine is stored in a wooden barrel of 2250 litres volume and frequently drawn (four times) it absorbs the following amount of oxygen (in ml l^{-1}) during the first year: through the free surface, 18; through the pores of the wood, 3; during the drawing, 14; total, 35. In subsequent years of storage the wine absorbs the following amount of oxygen (in ml l^{-1}) when drawn twice without access of air: through the free surface, 18; through the pores, 3; during the drawing (depending on the method of manipulation), 1–8; total 22–29.

As is evident from the data, oxidation is mainly a consequence of the evaporation of wine. Hence, if oxidation is to be prevented, the formation of free space above the wine surface should be prevented. This can be achieved either by a regular addition of wine or by its storage without access of air in tanks or cisterns.

The effect of oxygen on wine during maturing

The degree of oxidation of wine is determined by calculating the ratio of dissolution rate and the binding rate of oxygen. If the wine surface is exposed to air, the rate of dissolution of oxygen is higher than the rate of its binding. Under a restricted access of air the rate of diffusion is lower than the rate of reaction.

Kocherga (1949) called this ability the oxidation ability. He expressed the index of oxidation ability in oxygen units, mg l^{-1}, and called it the oxygen number. Kocherga's oxygen number represents the amount of oxygen dissolved in oxides and of oxygen bound in the salts of metals. Under these conditions, however, oxidation takes place much more slowly than in the presence of air oxygen.

Each wine needs a certain amount of oxygen for its development. This amount differs in different wines and depends on the type of wine. White wines usually mature in wooden barrels. During maturing they are drawn two or three times and thus enriched in oxygen. This treatment supports the maturing and purification. The wine assumes a balanced taste and clarity.

White wines gain optimum quality relatively quickly, within one or two years. Prolonged storage in barrels very much impairs the quality, because the wines lose their harmony and freshness under the effect of oxygen and assume an unpleasant 'aged' or 'senescent' taste. Therefore it is recommended that white wines be stored in barrels for a short period only and then allowed to mature without access of air in tanks or bottles. Defects in the clarity of wine can be eliminated by the addition of various clarification agents, which is a milder treatment than prolonged storage in wooden barrels. With a few exceptions these measures concern all white wines.

The exceptions are wines which need oxygen for their special development, for example Tokay and Madeira wines. During maturing they are kept in small wooden barrels and therefore they are exposed to a stronger evaporation and stronger oxidation. These wines contain a high percentage of ethanol, and a special taste, bouquet and full golden-yellow colour is formed under the effect of oxygen.

Red wines are substantially improved under the effect of oxygen. Therefore their oxidation is not restricted, but enhanced. The wines are allowed to mature in wooden barrels and even prolonged storage does not harm them. Red wines change taste and colour under the effect of oxygen, they become more harmonious and acquire the bouquet of old yellow wines; this is especially appreciated in red wines. Oxidation also enhances the process of precipitation of solid particles, which gives wine a greater clarity and stability in bottles.

Oxidation is also encouraged in the production and maturing of dessert wines; with higher temperatures the correct hue of the dessert wine is obtained, for example of Madeira.

It follows that oxidation has a great effect on the maturing of wine. Although it is generally known that various chemical and biochemical processess take part in the maturing of wine, the access of oxygen to wine, or its restriction, are of special importance. It makes a big difference whether the wine is aerated rapidly or slowly. Rapid aeration usually takes place during manipulations in cellars, i.e. drawing and filtration, during which a certain amount of oxygen enters into the wine. In this case the rate of dissolution of oxygen is higher than the rate of its binding. During slow oxidation, which takes place when oxygen enters the barrel through its pores, the rate of binding of oxygen is higher than the rate of its dissolution.

Rapid saturation of wine with oxygen or aeration has a negative effect on the quality of wine and it leads to loss of bouquet and often an unpleasant flat taste. The aftertaste of air which wines acquire during manipulation with air very much increases at elevated temperatures. However, it does not persist in the wine. If wine is stored under exclusion of air, the wine reassumes its properties. The ability to get back the taste which was damaged under the effect of oxidation is different for different wines.

In young wines the restoration of taste and aroma takes place relatively rapidly and the wine reassumes its original harmony within a few weeks. However, rapid oxidation of old good quality wines is more dangerous, since their bouquet disappears very rapidly under the effect of oxygen. Flat or stale old wines can regain their original bouquet only with great difficulty and after a prolonged time. Therefore all manipulations with wine should be carefully conducted and kept to a minimum.

Slow oxidation generally has a favourable effect because it co-acts in various chemical and other processes by which the wine assumes its bouquet and harmony. The oxidation of wine is affected by its chemical composition, especially by the presence of substances with a strong tendency to oxidation or which act as catalysts in oxidation processes. Tannins and pigments are very easily oxidized. According to Gerasimov (1952) tannin takes part in oxidation in two ways. On the one hand, it co-acts in the oxidation of wine and thus plays the role of a catalyst; on the other hand it acts by decreasing the oxidation rate of other substances after its own oxidation. In red wines the oxidizability of tannin prevents other oxidations and thus the loss of colour.

Sulphurous acid has a similar effect. It is a substance added to wine which is rapidly oxidized. In oxidation oxygen first attacks the sulphurous acid, with which it is combined, and cannot then oxidize other substances in wine.

It was observed that oxidation takes place better in the presence of catalysts – metal salts and peroxidase. The salts of iron and copper accelerate oxidation, which would be weak without them.

Methods of preventing contact of wine with oxygen

Both must and wine can be oxidized. The more solid particles a must contains, the more rapidly it is oxidized. Filtered musts do not brown on aeration and do not consume the added oxygen. This is because some polyphenols and other oxidizable substances are eliminated with the solid particles. During fermentation yeast consumes dissolved oxygen and the wine is saturated with carbon dioxide. During the drawing of wine from the yeast sediment carbon dioxide is liberated and oxygen is dissolved. Even during other cellar manipulations, such as filtration, clarification and bottling, carbon dioxide is released and oxygen is dissolved.

A high content of oxygen in wine is undesirable, because it causes premature maturing, and loss of colour, bouquet and the agreeable fresh taste. Therefore wine should be protected from excessive contact with oxygen. There are many ways to prevent excessive oxidation of wine, and two examples are given.

(a) Storing the wine in an inert atmosphere which restricts the effect of air oxygen even when the storage vessels are not full. An inert gas is introduced under mild pressure into the upper part of the vessel. The volume of the gas is eqal to the volume of the wine let out. Several inert gases may be used for this purpose. The simplest and cheapest is