

WINE CHEMISTRY IS A LIMITING FACTOR OF WINE MANUFACTURE

By

Nader Shaker¹ , Salwa D.Rafael² and Ali A.Morsi³

¹Pesticide Chemistry Dept. College of Agriculture, University of Alexandria.&
Scientific Consultant of The Egyptian Vineyards Company[†] .Horticulture crop
processing Dept.,Food Technology Res. Institute(ARC).Alexandria.

[†]Egyptian Vineyards Company. Ganaclis . Behera.

Recived 12/1/2000 , Accepted 28/3/2000.

ABSTRACT

Grape is an economic fruit used fresh or as juice or dried to resin or fermented to wine. Good wine quality should be produced from good mature grape, by using optimum biotechnological means of specific yeast strain of *Saccaromyces cerevisiae* in optimum condition of fermentation process.

Precipitate problem has been raised in some botteled wines in the market. The judicious use of the manufactural fining agent in raw wine such as tetrapotassium hexacyanoferrate to reduce the excess of copper and iron from 0.125,36.03, to, 0.081, 4.99 ppm respectively. The other treatment is with polyclar to reduce tannin content from 1650 to 200 ppm. Then the bentonite is to be used to overcome the problem of high concentration of protein content from 1200 ppm to 640 ppm. After these treatments, the clearance of fining process will be effecient and all used materials will be acceptable.

Lastly, different component for white wine" Karia & Batalsa" and rose wine "Robi" were investigated in cloudy and cleared stored bottled

wine. The cloudy ones contained higher protein content (4100 ppm) in white wine brand and(5700 ppm) in rose wine brand with small differences in tannin, iron and copper content compared with cleared bottled wines.

INTRODUCTION

Grape is an economic agriculture product to be used either fresh or manufactured by drying to resin or fermented to wine. Wine has the capability to prevent coronary atherosclerosis in fat people due to its high content of phenolic compounds, and antioxidant properties which have an important role to inhibit the copper-catalysed oxidation of normal human low density lipoprotein (Frankel *et al* 1993).

Wine derives its general quality and chemical composition from grapes and from yeast fermentation which converts their juice to wine. The undesirable changes that denote wine instability were listed by Berg and Akiyoshi (1956), as browning or other color deterioration, (b) haziness or very slight cloudiness, (c) cloudiness, (d) deposits and, (e) undesirable taste or odour. Bentonite, one of the fining agents most commonly used in winemaking, effectively removes protein or peptide materials. Active carbon, gelatin, casein and poly (vinylpyrrolidone) assist in removing unstable tannins and other pigments. Methods for removing excess copper and iron cation to prevent copper and iron turbidities in wine by the addition of tetrapotassium hexacyanoferrate (Wencker *et al* ,1990). Meanwhile, to prevent deposition of potassium bitartrate can be carried out by passing wine through a sodium cation exchange resin (Rankine and Emerson,1963).

In this paper, a small scale fining tests in the laboratory was carried out before attempt to clarify commercial quantities of wine to determine the efficiency of fining agent to solve precipitate problem in some bottles of wine on store shelf.

MATERIALS AND METHODS

The manufacture of wine is carried out in the Egyptian vineyard company as the following flow system; Grape Bunches --> Stemming -->Crushing --> pressing (product after this step is called must) --> sterilization and add of SO_2 --> fermentation -> ripening and fining (product after this step is called raw wine). The raw wine is the final product of the last flow sheet without aging step.

First treatment for removing excess copper and iron cations to prevent copper and iron turbidities in wine by the addition of tetrapotassium hexacyanoferrate (Wencker et al .,1990). $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$, Lemon yellow crystals or powder, mild saline taste; effloresces on exposure to air. Soluble in water, insoluble in alcohol. Sp.gr. 1.853 (17 °C) mp. loses its water of crystallization when heated to 70°C; b.p.decomposes. ; laboratory reagents. Metals concentrations are detected by using Atomic Absorbtion apparatus (AOAC,1980).

Poly (vinylpyrrolidone) $(\text{C}_6\text{H}_9\text{NO})_n$ white free-flowing amorphous powder or aqueous solution. Soluble in water and organic solvents. Combustible with wide range of hydrophilic and hydrophobic resins Sp.gr. 1.23 - 1.29 bulk density 25 lb/ft³ . Hygroscopic; nontoxic (Grade; various M.Wt. 10000 - 40000 - 160000 360000), adhesives beer and wine clarification.Assist in removing unstable tannins and other pigments (CCD,(1976))and determined tannin according to Bajaj and Sharma method (1977).

The raw wine was mixed throughly with Bentonite,(A colloidal native hydrated aluminum silicate (clay) consists principally of montmorillonite $\text{Al}_2\text{O}_3 \cdot 4\text{SiO}_3 \cdot \text{H}_2\text{O}$. The color in the massive condition varies from yellowish white to almost black. It has the property of forming highly viscous suspensions or gels with not less than ten times its weight of water.) one of the fining agents most commonly used in winemaking, effectively removes protein or peptide materials at

concentration of 1 gm/l wine(Rankline and Emerson(1963)) .After these step protein content was determined according to Lowry method (1951).

Karia and Batalsa are trade marks of white wine product while Robi is trade product produce from red grape varity. The chemical analysis of must or wine were determined according to standard methods. Alcohols, acidity and sugar content were determined as mentioned in AOAC(1980). pH was measured by using pH-meter apparatus.

RESULTS AND DISCUSION

The chemical composition of must is significant in winemaking and wine quality du0ring the chemical and biological processes of fermentation. The transformation of organic substances such as sugar and nitrogenous substances yield many components that are limiting to wine quality (Gallander, 1973) .The ratio of every compound is very important, to the absolute content, to have a right indication of the best winemaking for the several varieties and the different kinds of wines. Therefore, It was necessary to determine the chemical composition of must which affect the wine stability. Table (1)

Table (1) : Chemical compositin of must components in percentage.

pH	Acidity	Protein	Sugar %	Tannin %	Metals%				
					Fe	Cu	Ca	K	Mg
2.85	%0.64	%0.005	19.97	0.05	0175.	20.	015.	00015.	0015.

As shown in Table (2;a&b) raw wine contained 1200 ppm protein ,1650 ppm tannin and pH 3.953 . However different metal

concentrations were 36.03, .081, 25.80, 1400, 39.80 ppm for Iron, Copper, Calcium, Potassium and Magnesium respectively . Raw wine was treated under laboratory condition with fining agents to be sure that the sequence of manufacture fining process was efficient and all materials used were accepted to do their role.

Table (2,a) : Effect of different manufacture treatment on raw wine.

treatment	pH	protein (mg/L)	Tannin (mg/L)
Raw wine	3.953	1200	1650
after treatment with			
1 -ferrocyanide	3.976	1200	1700
- polyclar	3.983	900	200
-bentonite	4.016	640	100

The fining treatment procedure had started by adding tetrapotassium hexacyanoferrate (Wanker *et al.* (1990, This treatment overcome the wine cloudiness problem which caused by colloidal complex formation involving cations particularly copper and iron. After that treatment concentrations were decreased from 36.03 to 4.22 mg/l for iron and 0.08 to 0.05 mg/l for copper,(Table (2,b)).

The excess of 10 mg/l iron and 0.5 mg/l copper in wine matrix may be susceptible to clouding or sedimentation as well as flavour deterioration by the strong catalytic and oxidative properties of these cations (Thoukis and Amerine,1950)

The next treatment in the finning procedure is polyclar treatment to reduce tannin content from 1650 to 200 mg/l (Table (2,a)). Tannins and pigments oxidation cause wine clouding and color change after exposure to air. These changes are aggravated by phenolase and poly phenol oxidase which, in small concentration, is normally present in grapes (Amerine and Joslyn, 1970).

Table (2,b): Changes in metals content in mg /l for grape raw wine due to different manufacture treatments.

Treatment	Iron	Copper	Calcium	Potassium	Magnesium
Raw wine	36.03	0.081	25.80	1400	39.80
After treatment with					
-1ferrocyanide	4.22	0.055	24.11	1400	42.00
-2polyclar	5.12	0.075	25.73	1600	42.20
-3bentonite	4.99	0.125	24.60	1200	34.60

Then the the prepared bentonite was added to the wine sullary, which assisted to reduce protein content of wine from 1200 mg/l to 640 mg/l as shown in Table(2,a). The optimum protein content is not more than 848 mg/l (Blade and Boulton, 1988). Protein sarve as nuclei about which copper and iron salts deposit and form clouds on denaturation by heat, cold or prolonged aging of wines. Protein clouds may be also due to the results of protein-tannin complex formation in the presence of traces of heavy metals (kean & Marsh, 1956).

Table (3,a) : Determination of pH , protein and tannin in different grape wine brands.

Treatment	pH	protein)mg/L(	Tannin)mg/L(
White wine			
Karia	3.761	3100	240
Batalsa	3.761	4100	256
Karia	3.84	520	160
Batalsa	3.40	590	218
Rose wine			
Robi	3.682	5700	258
Robi	3.583	670	312

This study was carried out to emphasize precipitate particles in some bottled wines and focus on the main components which is responsible for this problem . So, the experimental data for white wine (Karia & Batalsa) and rose wine “Robi” were investigated to determine the different parameters in cloudy (the ones which show cloudiness and small flacuated precipitate materials inside bottles) and clear bottled wines. The data in Table (3,a&b), shows that cloudy botteled wines contained mainly high concentration of protein and small differences in tannin , iron and copper content compared with cleared botteled ones. In general the slight differences in some components in cloudy and cleared bottled wines were due to the influence of type of soil, climate, agronomical and varity characteristics (Freeman & Kliewer ,1983 and Larrechi *et al* , 1987). The cloudiness and precipitation in bottles on the

shelf are due to the changes of pH and its effect on chemical and physical condition of this high amount of protein in wine.

Table (3,b): Changes in electron conductivity, metals content and salt concentration in ppm for different grape wine brands.

Treatment	Iron	Copper	Pot.	salt conc	EC
White wine					
Karia	7.90	0.109	282	1.88×10^{-4}	185.6
Batalsa	5.45	0.131	317	2.11×10^{-4}	189.6
Good batch of Karia	620	0.103	280	1.67×10^{-4}	176.4
Batalsa	5.20	0.112	312	1.90×10^{-4}	171.5
Rose wine					
Robi	5.90	0.123	350	2.2×10^{-4}	190.6
Good batch of Robi	6.20	0.130	600	2.0×10^{-4}	186.2

Meanwhile, the high protein content may be due to, the use of non-mature grape which have high amount of non-developed protein. Moio & Addeo (1989) and Kallay (1992), suggested that the ratio between fructose to glucose content in this non-mature grape was more than mature one which emphasize high content of keto-saccharides which increased the activity of lactic acid bacteria than the yeast activity. The high action of lactic acid bacteria would increase the acidity and will also increase the ability of protein content to reach its isoelectric point and encourage protein precipitate in bottles.

Also, in non-mature grape the activity of maleic acid bacteria is higher than activity of tartaric acid bacteria which lead to undesirable

fermentation process. However besides that the high amount of yeast cells used in fermentation could leave high content of dead cells as a source of protein which could clear the higher amount of protein in wine more than in grape itself. This increase a production of small fragments in limited proteolysis conditions (Karasavova *et al*, 1993) .

In conclousion with present technology, such clouds or hazes were caused by grape or yeast proteins, peptides, unstable grapes pigments, tannins and some metals may be assisted in their separation from wine by the judicious use of small amounts of fining agents which adsorb or combine chemically and physically with the haze particles or colloids or neutralize their electric charges causing them to agglomerate and gravitate to the bottom in a reasonable time. To reach brilliant and clear wine with high quality must be start with good grape quality.

REFERENCES

- AOAC(1980)., Official Methods of Analysis of The Association of Official Analytical chemistry. William Horwitz, Editor, Eleventh Edition, 1970, Published by the AOAC, P.O.Box 540 Benjamin Franklin Station ,Washington ,DC 20044
- Amerine,M.A. and M.A.Joslyin (1970)., Table wines; The technology of their production , 2nd ed., University of California , Berkeley and Los Angeles. c.f.Chemistry of winemaking -Congress by American chemical Society, Division of Agricultural and Food Chemistry, edd by Webb, Albert Dinsmoor pp311.
- Bajaj, K.L.; and A.K.Sharma (1977)., A colorimetric method for the determination of tannins in tea Mikrochimica Acta pp 322 - 325.
- Berg .H.W and M.Akiyoshi (1956).,Some factors involved in browning of white wines. Amer.J.Enol.;7: 84-90.
- Blade,W.H.,and R.Boulton (1988)., Adsorption of protein by bentonite in model wine solution . American Journal of Enology and Viticulture , 39(3): 193 - 199.

- CCD,(1976)., The condensed Chemical Dictionary 9th eddition.
Published by Van Nostrand Reinhold company. New York,
London, Atlanta pp 96 - 707 - 713.
- Frankel,E.N; J.Kanner; J.B.German; E.Parks and J.E.Kinsella
(1993).,Inhibition of oxidation of human low density protein by
phenolic substances in red wine. The Lancet. 341 : 454 - 457. ,
- Freeman,A.U., and W.M.Kliwer (1983), Effect of irrigation,crop level
and potassium fertilization on Carignane vines. II. Grape and
wine quality. American Jurnal of Enology and Viticulture, :34
(3): 197 - 207.
- Gallander,J.F.(1973)., Chemistry of grapes and other fruits as the raw
materials involved in winemaking, c.f.Chemistry of winemaking
- Congress by American chemical Society, Division of
Agricultural and Food Chemistry, edd by Webb, Albert
Dinsmoor.pp 11-49.
- Kallay,M., E.Szovenyi and G.Bardi (1992)., Comparison of wine treating
materials and their effect on the chemical composition of the
wine. Magyar- Szolo es Borgazdasag. :2(5) : 3 - 6.
- Karasavova,M., B.Shopova , M.Kr'steva and L.Jotova (1993).,
Hydrolysis of wine proteins by means of pepsin immobilized to
ultrafiltration membrane Biotechnology and Biotechnological
Equipment .,7(3): 45 - 51.
- kean,C.E.and G.L.Marsh.(1956)., Investigation of copper complexes
causing cloudiness in wine. II Bentonite treatment of wines.
Food Technol. 10: 355-359.
- Larrechhi,M.S., M.P.Callao., F.X.Rius and J.Guasch (1987)., Na, K, Ca,
Fe and Cu content in red wines from Tarragona., Revista de-
Agroquimicay Tecnologia de-Alimentos , 27(1) : 53 - 59.
- Lowry, Rosebrough, Farr, Randall(1951)., Protein measurement with the
folin phenol reagent. J.Biol.Chem.193 :265.
- Moio,L.,and F.Addeo, (1989)., Isoelectric focusing of proteins from
musts and wines.,Vigne vini, 16(4): 53 - 57.
- Rankine ,B.C.and W.W.Emerson,(1963)., Wine clarification and protein
removal by bentonite. J.Sci.Food Agric.14: 685-689.

- Thoukis.G and M.A Amerine (1950)., The fate of copper and iron during fermentation of grape musts. *Amer.J.Enol.* 7:45-52.
- Wencker,D; B.Spiess; and P.Laugel (1990)., Influence of hexacyanoferrate (II) based treatment upon the elimination of heavy metal traces in wine.2. The case of cadmium. *Food Additives and contaminants.* 7(3):375-379.

الملخص العربى

كيمياء الانبذة عامل محدد لعمليات التصنيع

نادر شاكرا^١ ، سلوى دانيال^٢ ، على عباس^٣.

كلية الزراعة - جامعة الاسكندرية^١،

مركز البحوث الزراعية^٢ ، شركة الكروم المصرية^٣

العنب محصول اقتصادى يستخدم طازج او كعصير او مجفف فى صورة زبيب او مخمر كنبذ. للحصول على انبذة ذات صفات جيدة يجب استخدام اعناب جيدة فسى وجود البكتيريا المناسبة من صنف ساركوميسيس سيرفيمى وفى ظل ظروف قياسية.

تظهر مشاكل الترسيب فى بعض الزجاجات فى الاسواق ، وتم دراسة كيمياء عملية الترويق التى تتم على للنبذ الخام اثناء تصنيعة و ذلك باستخدام فيرو سيانيد البوتاسيوم لتخفيض الزيادة فى تركيز النحاس من ١٢٥ ر.مجم / لتر الى ٠.٨١ ر.مجم / لتر . بينما ينخفض تركيز الحديد من ٣٦٠٣ ر.مجم / لتر الى ٤٩٩ ر.مجم / لتر . ثم يتم اضافة مركب البولى كلار لتخفيض محتوى التانين من ١٦٥٠ الى ٢٠٠ ر.مجم / لتر . ثم تم اضافة مركب البتونيت لتخفيض التركيز العالى للمحتوى البروتينى من ١٢٠٠ الى ٦٤٠ ر.مجم / لتر ، ظهر بعد ذلك كفاءة عملية الترويق على النبذ الخام ليصبح لامع و شفاف و تصبح المركبات المستخدمة تم التخلص منها وتأثيرها مقبولا..

تم دراسة سبب ظهور رواسب فى الاسواق لأصناف النبذ البيضاء (قرية و بطالسة) و فى اصناف النبذ الروز (روى) و ذلك بتحليل الانبذة الموجود بها رواسب مقارنة بعينات جيدة من نفس الصنف . اوضحت النتائج ان الزجاجات العكرة بها تركيز عالى من المحتوى البروتينى يصل الى ٤١٠٠ ر.مجم / لتر بالنسبة لأصناف البيضاء و ٥٧٠٠ ر.مجم / لتر بالنسبة لأصناف الروز مع وجود بعض الاختلافات فى محتوى التانين و الحديد و النحاس و ذلك بالمقارنة بالعينات الجيدة.