

A Research Note DEPENDENCE OF FRUIT-BERRY WINES' STABILITY ON THE CONTENT OF MINERAL AND NITROGENOUS COMPONENTS

INTRODUCTION

THE INCREASED USE of metallic apparatus and capacities in wine-making result in richer content of iron salts, both in wine materials and in the finished product. Iron in wines is found in an ionic state, as in ferric (Fe⁺⁺⁺ and ferrous (Fe⁺⁺) salts (Arjun, 1966; Bergner and Lang, 1970). The formation of precipitate (Cass) does not depend solely on its iron content. Acids in wines are known to form soluble complexes with trivalent iron which prevents precipitate (Cass) formation. Conversely, iron precipitate (Cass) is intensively formed in a medium of sufficient protein content. Thus in fruit-berry wines, there are substances promoting both the decrease and disturbance of stability.

Since fruit-berry juices contain few nitrogenous substances, it was very im-

portant to find the dependence of fruit-berry wines' stability on the content of iron, organic acids and proteins (Gorinstein et al., 1971). In apple juice the natural nitrogen content is hardly sufficient for sugar fermentation which yields 5-6% vol alcohol. Wine-making experience elaborated modes of incorporating additional nitrogenous nourishment to complete the process of fermentation. It is quite natural that additional incorporation of nitrogenous substances results in the disturbance of stability. Thus the necessity arose to establish an optimum rate of additional nitrogenous nourishment which would cause no wine stability disturbance but would assist completion of the fermentation process. A series of experiments were carried out with this purpose in view.

berry, cherry, currant, fruit wines, red sweet wine, white sweet wine, Yantarnoye and Yubileynoye, produced by the experimental wine-making factory "Anyksci Vynas," were prepared from high acidic juices diluted with water by adding 27 gr/100 ml sugar, with fermentation lasting 70-100 days. All analyzed wine samples, except apple-wine, were prepared by combination.

Standards for comparison of wines were the same drinks clarified by filtering masses "Kineshma" (control) and "Evlakh" (test) (Gorinstein, 1970). Filtering masses "Kineshma"/6.6% turbidity of standard solution and "Evlakh"/1.9% turbidity of standard solution, distinguished by its filtering ability, were manufactured from raw materials of different compositions. "Evlakh" filtering mass was made at the Lvov Brewery Firm "Kolos" (Ear) by Gorinstein (1968; 1970). Iron was determined spectroscopically in wines by methods of Steiner and Oliver (1963); Bukharov and Mekhuzla (1964). Common nitrogen was found by the micromethod of Duma and Kjeldahl; (Gorinstein et al., 1971; Bulgakov, 1959; Klimova, 1967; Strukova and Fedorova, 1966; Fedoseev and Osadchii, 1969); protein nitrogen by deposition with hydrate of copper oxide; amino ni-

EXPERIMENTAL

THE OBJECTS of this investigation were fruit-berry wines. The fruit-berry wines apple, straw-

Table 1—Physico-chemical indices of fruit-berry wines

Qualitative I indices	Apple wine				Cherry wine				Currant wine			
	Before clarification	Control	Test	Bentonite	Before clarification	Control	Test	Bentonite	Before clarification	Control	Test	Bentonite
Iron, mg/liter	48.9	42.3	31.4	46.5	38.3	27.6	27.3	27.9	28.5	23.4	16.5	24.8
Nitrogen, mg/liter												
Common	86.5	75.4	75.1	75.5	134.4	118.3	118.1	118.5	93.4	86.3	81.4	85.7
Organic	50.4	46.8	46.5	46.6	81.3	75.6	79.3	80.2	67.3	52.7	49.6	51.0
Protein	38.9	33.5	33.3	33.4	45.4	36.2	30.3	32.4	48.0	41.7	39.8	43.3
Amine	15.7	11.8	11.7	11.9	16.8	14.3	11.7	12.0	15.7	12.6	10.7	11.2
Colloids, mg/liter	520.3	400.1	399.9	400.2	1103.3	872.4	851.0	879.4	400.7	354.7	572.1	280.5
Tannic & Dyeing substances, mg/liter	430.70	364.70	364.60	364.81	749.00	644.50	638.25	641.00	146.10	138.4	140.2	116.75
Dry substances mg/liter	578.20	503.42	481.03	499.10	872.02	794.52	775.40	789.31	344.00	331.14	305.00	318.40
Pectinic acid mg/liter	0.410	0.365	0.362	0.364	0.280	0.250	0.220	0.246	1.472	1.398	1.372	1.348
Insoluble ash, mg/liter	7.70	6.69	6.67	6.70	8.00	7.35	7.21	7.42	33.09	32.14	32.96	27.41
Soluble ash, mg/liter	19.2	18.1	18.2	18.3	20.9	17.6	17.1	17.4	25.5	23.6	24.8	18.3
Acidity, %	—	4.9	4.7	5.8	—	9.1	9.1	9.1	—	7.4	7.2	7.3
Stability, months	—	5.0	5.1	4.9	—	4.0	6.0	5.4	—	5.0	5.0	4.8

Table 2—Dependence of the process of fermentation (alcohol) of apple juice and wine stability from additional nitrogenous nourishment

Composition of nourishment	Common nitrogen, mg/liter						Wine		
	Juice	Beginning of fermentation	Additional nitrogenous nourishment	After addition of nitrogen	At end of fermentation	Wine material	Common nitrogen mg/liter	Alcohol %	Stability months
KC + (NH ₄) ₂ HPO ₄	218.6	98.6	100	198.6	142.3	91.4	77.4	12.7	4.3
	218.6	98.6	200	298.6	150.4	93.5	80.3	13.1	4.4
	218.6	98.6	300	398.6	162.7	95.6	85.9	13.5	4.7
	218.6	98.6	400	498.6	169.5	99.7	89.8	13.7	4.9
KC + (NH ₄) ₂ SO ₄	218.6	98.6	100	198.6	143.5	93.6	79.4	11.8	4.3
	218.6	98.6	200	298.6	151.7	95.8	82.1	12.0	4.6
	218.6	98.6	300	398.6	164.2	97.3	87.9	12.4	4.7
	218.6	98.6	400	498.6	174.8	101.3	91.5	12.7	4.9
KC + NH ₄ Cl	218.6	98.6	100	198.6	142.0	90.5	74.9	12.8	4.7
	218.6	98.6	200	298.6	149.3	91.8	76.5	12.9	4.8
	218.6	98.6	300	398.6	161.5	94.3	81.3	12.1	4.9
	218.6	98.6	400	498.6	167.6	98.5	84.5	13.9	5.0
KC + (NH ₄) ₂ HPO ₄ + (NH ₄) ₂ SO ₄	218.6	98.6	100	198.6	140.5	87.9	73.5	13.1	5.4
	218.6	98.6	200	298.6	147.3	89.8	75.4	15.2	6.0
	218.6	98.6	300	398.6	157.3	93.5	79.7	14.3	5.3
	218.6	98.6	400	498.6	162.9	97.6	81.5	14.5	5.1
KC	218.6		0	98.6	85.1	63.7	57.3	9.3	3.0

trogen by means of copper; and organic nitrogen by K₂S₂O₈ (Gertner and Gidinic, 1965). Colloids were determined according to GSE (Dumanskii et al., 1936); dry, pectic substances and insoluble and soluble turbidity gravimetrically; tannic, dyeing substances and acidity titrimetrically; and colloid-protein stability and alcohol by conventional methods (Fertman and Gorinstein, 1970; Nilov and Skurikhin, 1967).

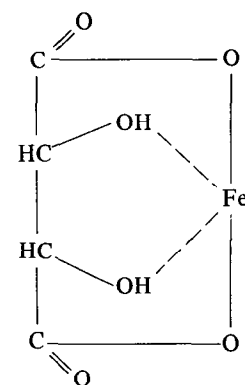
RESULTS & DISCUSSION

THE CONTENTS of iron, common, organic and amine nitrogen protein, alcohol, colloids, dry, tannic, dyeing, pectinic, ashen substances and acidity were studied. The data obtained show that before clarification three groups of wines could be distinguished according to the concentration of the main components underlying the terms of stability: (1) wines with high content of iron; (2) common nitrogen; and (3) wines with mean numbers both of iron and common nitrogen. Examples of these groups are apple, cherry and currant wines, respectively (Table 1).

It was interesting to follow the dynamics of indices studied after the clarification of fruit-berry wines by filtration through filtering masses "Kineshma," "Evlakh" and bentonite. The data are given in Table 1. Analyses of these data show, that after clarification, typical distinctions of qualitative indices of three groups of wines continue to change: in apple-wine the highest concentration of iron is retained; in cherry-wine that of

common nitrogen. Interesting data were obtained by analysis of the relation of stability terms of wines containing iron and common nitrogen. According to the laws of formal logic it could be expected that in wine with high iron content the stability would be the least. However, the data obtained experimentally contradicted this. In the sample of apple-wine clarified by bentonite, the iron content (true to statistics) is higher than in sample controls and tests (in both cases $P < 0.001$; $P =$ probability of distinction). With approximately the equivalent quantity of common and protein nitrogen, it is in the apple-wine sample, clarified with bentonite, that the least stability could be expected. However, in our experiment, wines clarified by different means have the same stability. This implies that other factors affecting the stability exist (Nilov and Skurikhin, 1967; Rodonulo, 1971; Ogorodnik and Dranovskaya, 1970). Indeed, despite the high concentration of iron in the apple wine clarified by bentonite, the presence of considerable amounts of organic acids (acidity, 5.8% and iron 46.5 mg/liter) prevents stability decrease. This is explained by the fact that malic and citric acids readily form soluble complexes preventing the formation of iron precipitates (Cass). According to Nilov and Skurikhin (1967), tartaric acid in wine with Fe⁺⁺ oxidizes COOH-CHOH-CHOH-COOH-2H COOH-COH=COH-COOH. But this process is weaker, because iron (II) is oxidized to iron (III) and has no catalytic force. But

iron in wine forms the following complex (Nilov and Skurikhin, 1967):



This complex is possessed with a catalytic force and prevents transition of Fe^{II} to Fe^{III} (Nilov and Skurikhin, 1967).

It is known that the velocity of redox reactions depends upon the acidity of the media. In acid media, that is in wine, oxidizing processes took place more slowly than in neutral and alkaline media. It is obvious that while the oxidation process is necessary for the ripening of wine, results may also be undesirable. For example, in oxidation the possibility of the formation of tannin-protein combinations falling out in the sediment and the acquisition of stable transparency in wine was stronger, so the bitter taste of tannides was softer. But simultaneously the oxidizing of the amino acids results in deterioration of aroma and taste.

According to Table 1 the largest amount of common nitrogen is found in cherry wine. In samples of this wine clarified with different types of filtration masses and bentonite, essential distinctions in content of iron, common nitrogen and in acidity, indices were not found. With equivalent values of indices influencing the terms of stability, one could expect it to be identical for all samples of cherry wine. Experiments show, however, that the highest stability is found in cherry wine test (6.0 months), somewhat less in the wine clarified with bentonite (5.4 months), and still less in wine control (4.0 months). By qualitative analysis it was found that in wines with equal amounts of common nitrogen there were different contents of protein nitrogen (Table 1). Thus it can be concluded that wine stability is in reverse dependence from the contents of protein (not common) nitrogen. Concluding the analysis of Table 1, it must be noted that the best qualitative indices are possessed by wines clarified with the filtration mass "Evlakh," with wines clarified with bentonite somewhat worse.

The protein content of bentonite-treated wines decreases considerably while stability increases (Table 1). But in comparing wine test to wine bentonite, wine bentonite has a little more protein. The adsorption ability of the filtering mass "Evlakh" is better than bentonite.

The amount of common nitrogen was determined in apple, cherry and red currant juices. Qualitatively and quantitatively different protein nourishment was incorporated into each juice. Again common nitrogen was determined and repeated at the end of fermentation in wine material and in finished wine. The data were compared with alcohol content and terms of stability (Table 2). Analysis of

data obtained enable us to establish optimum additional nitrogenous nourishment both quantitatively and qualitatively. Optimum nitrogenous nourishment was considered the one which in minimum amounts ensured completion of the fermentation process (according to alcohol) and the longest terms of stability (Table 2).

CONCLUSION

THUS WE CAME to the conclusion that the addition of nitrogenous nourishment to the high nitrogenous cherry juice, is superfluous. Optimum nitrogenous nourishment for apple juice is a mixture of phosphate and ammonium sulfate in the amount of 200 mg/liter and for currant juice, ammonium phosphate in the amount of 100 mg/liter which is considerably below conventional rates.

The results of the investigation show that fruit-berry wines, like beer, are subject to common regularities of retaining colloid-protein stability of ethanol media (Gorinstein, 1968).

REFERENCES

- Arjun, B. 1966. Iron and copper in vini. *Harpers Vine & Spirit Gasette*: 60.
- Bergner, K. and Lang, B. 1970. Versuche zur Anwendung der Röntgenfluoreszenzspektrographie in der Weinanalyse (Fe, Cu, Zn, Mn, Br). *Deutsche Lebensmittel-Rundschau* 66(5): 157.
- Bulgakov, N. 1959. The determination of protein substances. *Proizvodstvennyi laboratornyi Kontrol solodorashcheniya i pivovareniya*: 214.
- Bukharov, N. and Mekhuzla, N. 1964. Opređenje metallov v vine metodom spektrograficheskogo analiza. *Metody issledovaniy vinodelii*: 31.
- Dumanskii, A., Kharin, S. and Maltsev, P. 1936. The determination of quantity of colloids in beer. *Kolloidnyi Zhurnal* 11(4): 261.
- Fedoseev, P. and Osadchii, V. 1969. Method of quantitative determination of nitrogen in the nitrogen-containing substances. *Izvestiya Vysshikh Uchebnykh Zavedenii, Tekhnologiya legkoi promushlennosti*: 2.
- Fertman, G. and Gorinstein S. 1970. Determination of colloid-protein stability of fruit-berry wines. *Kharchova Promuslovist'* 5: 32.
- Gertner, A. and Gidinic, V. 1965. Određivanje ukupnog organskog dusika u razrijedenim vodenim otapinama. *Acta Pharmaceutica Jugoslavica* 4: 209.
- Gorinstein, S. 1968. Beer filtration with improved filtering mass. *Fermentnaya i spirtovaya promushlennost* 1: 14.
- Gorinstein, S. 1968. The investigation of the chemism of clarification of ethanol media. *Autoprecis*: 19.
- Gorinstein, S. 1970. The way of obtaining the filtration mass for ethanol media clarification. Author's certificate USSR, Moscow, 273138.
- Gorinstein, S., Venskyavichus, J. and Makshtyalene, Z. 1971. The change of common and organic nitrogen in fruit-berry wines. *Vinodelie i vinogradarstvo Moldavii* 4: 33.
- Klimova, V. 1967. The determination of nitrogen. *Osnovnye mikrometody analiza organicheskikh soedinenii*: 71.
- Nilov, N. and Skurikhin, J. 1967. The organic acids; the colloids of wine; The nitrogen substances; The mineral substances; The active acidity; The transformation of organic acids; The transformation of nitrogenous substances. *Khimiya vinodeliya. Pishchevaya promushlennost*.
- Ogorodnik, S. and Dranovskaya, T. 1970. The turbidity of wines called by content of metals. *TSINTIPISSHCHEPROM*.
- Rodonulo, A. 1971. The formation and transformation of nitrogenous substances at alcohol fermentation; Metabolism of organic acids by wine yeast; The transformation of organic acids at fermentation of wine material (must) and formation of wine; The role of organic acids in technology of manufacture and at stability of wine. *Biokhimiya vinodeliya. Pishchevaya promushlennost*.
- Steiner, R. and Oliver, R. 1963. Spectrochemical determination of trace metals in beer. *Amer. Soc. Brew. Chem. Proc.*: 111.
- Strukova, M. and Fedorova, G. 1966. The determination of nitrogen by Kjeldahl method without distillation of the ammonia with utilization of sodium tetraphenylboron. *Zhurnal analiticheskoi Khimii* 4(21): 509.

Ms received 5/31/73; revised 7/23/73; accepted 7/25/73.

The author is grateful to Professor K. Mikhalevich (Lvov Polytechnic Institute) for enabling him to carry out most of the experimental work at his laboratories. The author thanks M.Z. Makshtyalenc who supported this work by contract; M.L. Kiselyova for skillful experimental assistance; and Prof. B. Kirson (The Hebrew University of Jerusalem) for his interest in the work.