STUDIES WITH BRANDY. I. pH [1]

J. F. GUYMON, N. E. TOLBERT, AND M. A. AMERINE
University of California, Davis, California

(Received for publication, November 28, 1942)

Although there is fair agreement as to the nature of the titratable acidity changes during the aging of distilled spirits in wooden containers, there is comparatively little information concerning the related pH fluctuations. Only recently have there been any detailed studies for whisky. Liebmann and Rosenblatt (1942) have found a knowledge of the pH useful in controlling the precipitation of metals from whisky. They reported that the change in pH during aging was a direct maturing characteristic of the whisky. They also showed that the pH tended to decrease during the first 24 months of storage. The pH of seven whiskies varied from 3.68 to 4.78, the highest value being in a new whisky. Valaer (1940) has studied the pH of commercial samples of Scotch whisky. In 97 samples of Scotch he found the pH to range from 4 to 4.78, averaging 4.34. In 70 American-Scotch type whiskies he found the pH to range from 4 to 6.22, averaging 4.81. In 10 samples of Irish whisky the pH ranged from 4.25 to 5.06, averaging 4.55. In rum Valaer (1937) found the pH to vary according to the source, exceeding 5 for Cuban and Puerto Rican rums. The pH of rums distilled in this country was lower. During aging there was generally a decrease in pH.

Valaer (1939) has also published the most extensive data on the pH of brandy. In 113 samples, primarily of post-prohibition California brandy, he found the pH to range from 3.85 to 5.67, averaging 4.42.[2] The low pH values of young brandies were attributed to the use of distilling material high in sulfur dioxide. A portion of the sulfur dioxide passing through the still is dissolved in the distillate and is slowly oxidized from sulfurous acid to sulfuric acid. Presumably this is not always the cause of low pH in brandies, for in 20 authentic French cognacs, in which the sulfate content owing to oxidation of sulfite is relatively low, the pH was found to vary from 3.76 to 4.98, averaging 4.14. In 25 Greek brandies the pH ranged from 3.28 to 5.77, averaging 4.41. Valaer also analyzed a number of apple, apricot, and peach brandies. In 85 apple brandies the pH averaged 4.67, in nine peach brandies 4.72, and in four apricot brandies 4.09. He also followed the pH change in seven grape brandies during aging. The pH dropped an average of 1.82 in four years in three brandies, but in four other brandies aged for two years the pH dropped only .60.

[1] This is the first of a projected series of articles on the composition of brandy. These studies were made under the direction of the senior author, but owing to the exigencies of war only this and a second paper on tannin can be published at the present time.

[2] pH's as low as 2.24 and as high as 7.97 were found in certain anomalous samples reported by Valaer in a private communication giving in detail the original data.

The original high pH of two of the samples aged for four years probably accounts for some of the difference.

It is therefore evident that the pH of commercial distilled spirits ranges from 4 to 5, that it tends to decrease during aging, and it appears that rum has a higher average pH than the other distilled spirits.

EXPERIMENTAL PROCEDURE

A Beckman pH meter was used for making the pH measurements and the titration curves. The instrument was regularly checked against standard buffer solutions. Schicktanz and Etienne (1937), in making whisky titration curves, indicated that dilution and other errors affect the accuracy of the pH measurements. Liebmann and Rosenblatt (1942), however, have found the glass electrode to give an accurate measure of the pH in 50 per cent alcoholic solutions up to a pH of about 8.

Brandies from three general sources were used. Ten samples were brandies submitted for judging at the 1939 Golden Gate International Exposition, hereafter called Exposition brandy. Unopened duplicate bottles were secured for analysis. Nineteen samples secured from the Growers Grape Products Association were produced in connection with the 1938 California grape prorate program.[3] These are called Prorate brandies hereafter and may be considered to give a representative picture of the composition of newly distilled, cut, caramelized California brandies. Eighty-four samples of brandy were produced in this laboratory during 1939 and 1940 in a 26-plate, 12-inch, Krenz-type, continuous column still. These brandies were produced from distilling material of known composition, were distilled under carefully observed and controlled operating conditions, were all cut to approximately 102° proof before barreling, and were aged at a constant temperature in cooperage treated in various ways. These brandies are reported as University brandies with their original cellar numbers.

EXPERIMENTAL RESULTS

The results of the analysis of the 10 Exposition brandies (Table 1) show a range from 3.38 to 4.47 in pH, averaging 4.10. Their total acidity is practically all volatile and ranges from .0193 to .0658, averaging .0404 per cent. There is no exact relationship between the titratable acidity and the pH except that with high titratable acidity the pH tends to be lower.

The pH and total acid determinations on the 19 Prorate brandies (Table 2) show a range in pH from 3.12 to 7.55, averaging 5.06. The total acidity averaged only .0083, and there was practically none in several of the samples, particularly in those with a pH exceeding 6. Some of

[3] The history of these samples is as follows: After the brandy produced in each run had been cut and colored, the storekeeper-gauger of the Alcohol Tax Unit took a sample from one of the barrels of the run. These samples were then sent to the association for organoleptic examination. A run usually consisted of 25 to 150 barrels. At the end of the season the unused portion of the samples from each of 19 distilleries, located in all parts of the state, were combined into 19 separate lots. Each lot represented an average of 15 different distillations made during the season, so that over 250 different distillations are represented in these composite samples.

these abnormally high pH's are probably due to the distillation of neutralized distilling material and the consequent lack of volatile acids in the distillate. The buffer capacity of new alcoholic distillates is so low that the addition of only small quantities of either acid or alkaline substances results in abnormally high or low initial pH; for example, use of alkaline water for cutting may result in high pH. Caramel syrups are not stable in alkaline solutions and the brandies with a high pH precipitated most of their caramel as a gummy, reddish mass. Newly distilled brandies with a pH below 4 are also abnormal. Valaer (1939) found a number of the young California brandies of very low pH and, as already mentioned, he

TABLE 1

Total Acidity and pH of the Exposition Brandies[1]

Number	Total acidity[2]	Volatile acidity[2]	pH
E-1	.0322	.0273	3.38
E-2	.0276	.0227	4.22
E-3	.0480	.0423	4.08
E-4	.0575	.0401	3.88
E-5	.0390	.0382	4.32
E-6	.0193	.0144	4.12
E-7	.0257	.0206	4.43
E-8	.0515	.0417	4.01
E-9	.0658	.0582	4.10
E-10	.0377	.0340	4.47
Average	.0404	.0340	4.10

[1] Proof ranged from 83° to 100°. [2] As grams of acetic acid per 100 ml.

TABLE 2

Acidity and pH of 19 Composite Samples of Young Brandies From the Prorate Brandies

Number	Number of samples in composite	pH	Total acidity[1]
P-1	14	5.08	.0036
P-2	14	3.28	.0216
P-3	15	7.50	.0004
P-4	12	7.43	.0010
P-5	19	3.88	.0098
P-6	15	3.60	.0272
P-7	15	6.45	.0009
P-8	?	4.40	.0058
P-9	14	6.30	.0013
P-10	16	3.12	.0314
P-11	14	4.85	.0017
P-12	15	4.11	.0055
P-13	16	7.55	.0005
P-14	15	4.28	.0068
P-15	11	4.72	.0023
P-16	15	6.17	.0020
P-17	14	3.52	.0114
P-18	13	3.32	.0234
P-19	16	6.65	.0004
Average	15	5.06	.0083

[1] As grams per 100 ml.

explained this on the basis of their high sulfurous-sulfuric acid content.

The analytical data for the 84 University brandies are summarized (Table 3). No sulfur dioxide was used in the fermentation of the distilling material for these brandies. Storage in five-gallon oak containers apparently speeded up the maturation as regards the volatile and total acids which became rather high. The pH is, however, not as low as that of commercial brandies which contain sulfurous-sulfuric acid and which are aged in 50-gallon barrels for approximately the same length of time.

During aging the pH of these brandies decreased, first rapidly, and after the first year more slowly. Originally the pH was approximately 5.

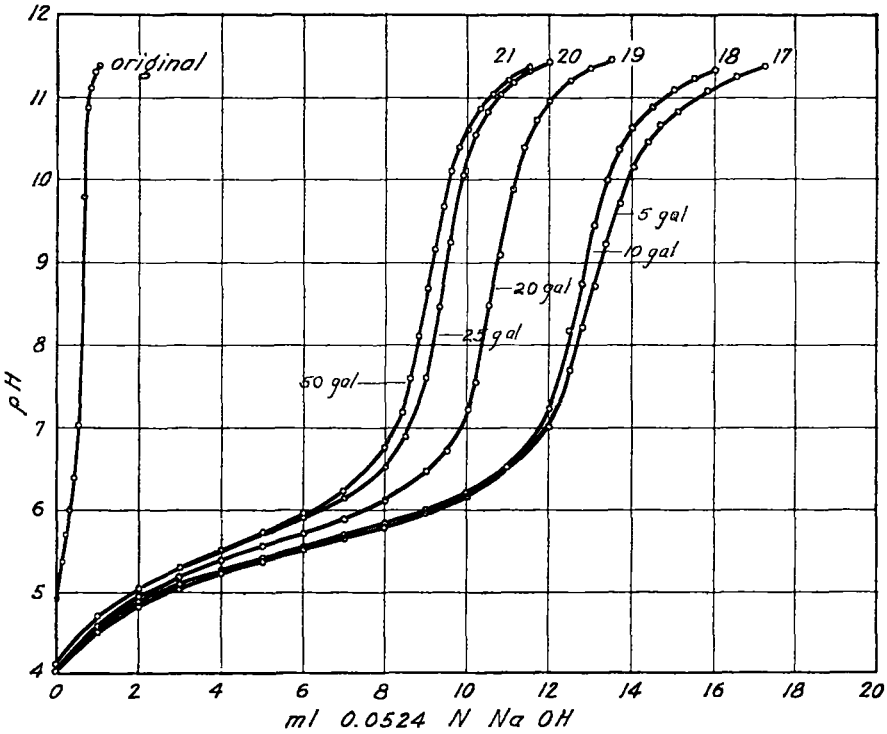

FIG. 1. Titration curves of the original brandy and of the same brandy after storage in five-, 10-, 15-, 25-, and 50-gallon containers.

During aging most of the brandies lost a full pH unit. In three special cases old wine, high in acetic acid, was distilled. The pH of the newly distilled brandy in these cases was 2.61, 3.78, and 3.91, and it increased during three years to 2.71, 4, and 3.98, respectively.

In the samples distilled from sound young wines the pH decreased and the shape of the titration curves changed during aging (Fig. 1). This change in shape of the titration curve during aging has been noted previously by Schicktanz and Blaisdell (1940) for whisky.

The data indicate that the larger the cooperage the less rapid the changes in pH and acidity. This is probably the result of at least three factors. The smaller barrels have a much greater surface exposed to the

TABLE 3

Influence of Age, Size, and Treatment of Barrels on Acidity and pH

University No.	Number of containers	Barrel size [1]	Barrel treatment [2]	Total acid (gm. acetic acid per 100 ml.)				Volatile acid (gm. acetic acid per 100 ml.)			pH			
				1939 [3]	1940	1941	1942	1940 [4]	1941	1942	1939	1940	1941	1942
1939 BRANDIES														
17	1	5	Rinsed with brandy	.0031	.0582	.0606	.0911	.0453	.0538	.0786	5.37	4.12	4.10	4.01
18	1	10	Rinsed with brandy	.0031	.0630	.0665	.0702	.0494	.0615	.0598	5.37	4.14	4.12	4.05
19	1	15	Rinsed with brandy	.0031	.0510	.0564	.0730	.0426	.0520	.0651	5.37	4.30	4.16	4.06
20	1	25	Rinsed with brandy	.0031	.0557	.0491	.0511	.0375	.0454	.0401	5.37	4.21	4.17	4.09
21	1	50	Rinsed with brandy	.0031	.0454	.0486	.0499	.0326	.0446	.0412	5.37	4.21	4.18	4.08
22	1	50	Charred; scraped out; rinsed with brandy	.0031	.0123	.0125	.0219	.0094	.0110	.0190	5.37	4.53	4.47	4.31
23	1	25	Two-year-old brandy barrel	.0031	.0162	.0168	.0304	.0129	.0147	.0243	5.37	4.72	4.70	4.45
27	1	5	Na_2CO_3 wash; soaked with brandy	.0031	.0529	0550	.0674	.0405	.0467	.0545	5.37	4.42	4.31	4.20
....	19	5	Rinsed with brandy	.0056	.0706	.0725	.0960	.0503	.0647	.0792	4.88	4.10	4.07	3.99
....	3	5	Steamed; soaked with brandy	.0034	.0618	.0665	.0859	.0436	.0595	.0678	5.40	4.11	4.10	4.00
1940 BRANDIES														
78	1	25	Steamed; soaked with brandy	.....	.0031	.0342	.0466	.....	.0312	.0415	.....	4.98	4.37	4.30
79	1	25	Old brandy barrel	.....	.0031	.0127	.0259	.....	.0115	.0237	.....	4.98	4.53	4.40
....	20	5	Boiled hot water; soaked with brandy	.....	.0057	.0666	.0971	.....	.0585	.0788	.....	5.01	4.12	4.08
....	29	10	Boiled hot water; soaked with brandy	.....	.0045	.0544	.0729	.....	.0498	.0653	.....	4.87	4.22	4.21

[1] In gallons. [2] All barrels were new unless stated otherwise. [3] Actual dates of withdrawal of sample, 1939 brandies; 1939 original brandy—Dec. 22 to Jan. 16, 1940; 1940—Aug. 15; 1941—Jan. 15; 1942—Jan. 19. 1940 brandies: 1940—Oct. 23 to Jan. 16, 1941; 1941—Aug. 4; 1942—Aug. 8. Note for the 1939 brandies that the time elapsed between the 1941 and 1942 analyses is one year, which is the same as that elapsing between the combined 1939, 1940, and 1941 analyses. [4] No volatile acid is given for the new brandy as it is approximately the total acid.

brandy per unit volume than the larger barrels. Therefore, more acidic compounds are extracted from the wood in the small containers. Moreover, the evaporation losses from small containers are more rapid so that greater amounts of the brandy are lost and larger air spaces develop in proportion to the total volume. Oxidation of alcohol to acetic acid is therefore accelerated. Finally, in the small containers, as the volume decreases more rapidly, there is a greater concentration of acidic materials. The final pH of the 1939 brandies stored in five-, 10-, 15-, 25-, and 50-gallon containers in 1942 was 4.01, 4.05, 4.06, 4.09, and 4.08. In 20 of the 1940 brandies stored in five-gallon containers the pH had decreased from an original average of 5.01 to 4.08 in 1942. The average original pH of 29 of the 1940 brandies stored in 10-gallon barrels was 4.87, but in 1942 it had dropped only to 4.21.

These differences in pH are closely paralleled by the changes in acidity. The reason for the slightly higher volatile acidity in the 50-gallon container compared with the 25 in the 1942 analysis is not apparent, since previously there was less volatile acidity in the brandy in the large container. It is possible that the bung on the 50-gallon barrel may have come loose during aging.

Pretreatment of the cooperage with sodium carbonate had a measurable effect. the pH of the brandy being higher than that stored in untreated cooperage. This was probably due to the neutralizing influence of the alkali on the wood since the barrels were very thoroughly washed with water after treatment. Rinsing and steaming the barrels one and a half hours and soaking them with brandy two or eight hours did not seem to make much difference in the pH changes. Used cooperage slowed down the pH change very materially.

In connection with this same study distillations at different proofs and from wines made of various varieties of grapes have been made. Neither the proof of distillation nor the variety of grape from which the distilling material was made appeared to have any influence on the total acidity or on the pH of the resulting brandy when cut and aged.

DISCUSSION

There is a lack of relationship between pH and titratable acidity in new brandies. Acetic acid is the predominant acid present and does, of course, have some buffer action. Schicktanz and Blaisdell (1940) have found the titration curve of aged whiskies to differ from that of young whisky, presumably because of the extraction of acidic substances from the wood during aging. The fact that the pH continues to decrease indicates that acetic acid is increasing since it has a pK lower than that of the other organic acids present.

The variability in the pH of newly distilled California brandies is remarkable. The excessive use of sulfur dioxide in the fermentation of the distilling material is reflected in the occasional low pH of new brandy and in the low pH of several of the aged brandies. The changes in pH in small cooperage are greater than that in large cooperage. The pH of sulfur dioxide-free brandies falls to approximately a pH of 4. It is not known whether this is true of all brandies. Crampton and Tolman (1908), how-

ever, found in whisky that the acid content approaches a maximum after three or four years in the wood. A similar equilibrium is apparently reached in brandy.

SUMMARY

The pH of 10 commercial, 19 newly distilled, and 84 experimental brandies was determined. Commercial brandies have a pH of 3.38 to 4.47 and average 4.10. Newly distilled brandies have pH's of 3.28 to 7.55, averaging 5.06. In the experimental brandies the pH decreased during aging. The decrease was larger and more rapid in small cooperage compared with large. Pretreatment of the barrel had a marked influence on the changes in pH if the barrel had been previously used or washed with sodium carbonate.

REFERENCES

CRAMPTON, C. A., AND TOLMAN, L. M., 1908. A study of the changes taking place in whiskey stored in wood. J. Amer. Chem. Soc. 30, 98-136.

LIEBMANN, A. J., AND ROSENBLATT, M., 1942. pH in distilled beverages. Assoc. Off. Agr. Chem. J. 25, (1), 163-168.

SCHICKTANZ, S. T., AND BLAISDELL, A. C., 1940. Determination of the total, volatile, and fixed acids of distilled spirits from potentiometric data. Assoc. Off. Agr. Chem. J. 23, 359-367.

———, AND ETIENNE, A. D., 1937. Acid content of whiskey. Ind. Eng. Chem. 29, 157-159.

VALAER, P., 1937. Foreign and domestic rum. Ind. Eng. Chem. 29, 988-1001.

———, 1939. Brandy. Ind. Eng. Chem. 31, 339-353.

———, 1940. Scotch whisky. Ind. Eng. Chem. 32, 935-943.