Silver

in the Artificial Aging of

The use of a process which consists of dispersing minute quantities of ionic silver in the liquid is described for the artificial aging of brandy.

Brandies given this silver treatment in the laboratory and held for about a week showed a mellowing effect and considerable change in flavor and aroma; the method may be useful for the quick aging of distilled alcoholic beverages.

There was a loss in aroma and flavor when brandies were silver-treated or stored around 45° C. Satisfactory results were obtained when brandies were silvertreated at lower temperatures or stored at temperatures from 0° to 37° C. Although there is a change in flavor and aroma brought about by the silver treatment, apparently no significant change, as indicated by chemical analyses, takes place in the acid, ester, aldehyde, or fusel oil content of the brandy.

THE quick aging of alcoholic beverages has engaged scientific workers all over the world. The shortening of the time necessary for the aging process has many economic aspects, since the holding of large quantities of liquor in storage is often a financial burden, and loss due to leakage and evaporation is likely to be serious. Any method which can be operated successfully to shorten this aging period is certain to be remunerative to those employing it.

Many methods have been advanced for the quick aging of alcoholic beverages, employing various materials and devices. These have been reviewed by Fain and Snell (2). Some of the methods have met with varying degrees of success in practice, but few of them have reached commercial importance. To be successful a method must be economical, effective, and without adverse effect upon the desirable qualities of a product.

In a preliminary experiment the authors found that, when minute amounts of silver were dispersed in a 100-proof alcohol-water mixture, a change similar to "aging" took place within a few days. A vanillin-like aroma was developed, and most of the raw alcohol flavor was lost, giving way to a flavor of rather smooth, delicate character. It was to study the effect of such a treatment on brandy and other alcoholic products that these studies were undertaken.

The authors of this article discuss only the chemical aspects of the subject, and the reader should therefore not infer that either the addition of ionic silver to liquors or the process used is necessarily recommended by the Department of Agriculture. The food and drug laws may restrict such additions entirely and/or may require special labeling.

Brandies

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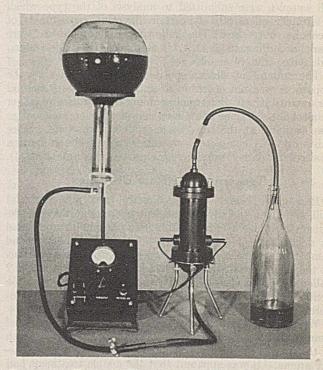


FIGURE 1. TREATING BRANDY IN AN EXPERIMENTAL-SIZE Apparatus

The apparatus used in these aging studies was a small experimental ionic silver sterilizer similar to those employed in water and vinegar sterilization (Figure 1). This apparatus consists of a hard rubber case holding two silver electrodes between which flows the product to be treated. The ionic solution of the silver is effected by inducing an electrical potential of approximately 1.6 volts of direct current between the electrodes and the liquid. This process has already been discussed by James (3). The maximum rate of flow of liquid through the apparatus was approximately 10 gallons (38 liters) per hour.

The various brandies used in these experiments were commercial products. The apple brandy used was 102 proof and the grape brandy 180 proof. The apple brandy was distilled from a pot still and, before being placed in barrels for storage, was passed through a quick ager. This apparatus consists of a small tank charged with toasted oak chips and wood charcoal through which the raw brandy percolates. In this treatment certain of the alcohol- and water-soluble constituents of the wood products are dissolved in the brandy and produce an effect similar to a longer period of natural aging in the wood. The term "quick aged" in this paper refers to this process and not to the silver treatment employed.

In order to determine the effect of this quick aging on the volatile esters and fusel oil of the brandies to be given the silver treatment, samples of the raw and quick-aged product were taken almost simultaneously. There is no significant change in either volatile ester, fusel oil, or acidity content due to passage through the oak chips in the quick ager; this result is in accord with the findings on whisky by Valear and Frazier (5), with the exception that they found a greater increase in acidity:

Apple Brandy	Esters Fusel Oil Acidity as Acetic				
Raw Quick-aged	$0.075 \\ 0.075$	$ \begin{array}{c} 0.100 \\ 0.098 \end{array} $	$\begin{array}{c} 0.031 \\ 0.035 \end{array}$		

An attempt was made to correlate the chemical analysis with the aroma and flavor, both before and after treatment. All samples were submitted to analysis of the type which determines quantitatively certain flavoring constituents of alcoholic beverages. The following determinations were made according to A.O.A.C. methods (1)—acids, esters, aldehydes, and fusel oil.

The amount of silver deposited in the brandies by the apparatus was not determined, since no satisfactory method for quantitatively determining minute quantities of silver in alcoholic solutions containing considerable organic matter was available at the time these studies were made. Since this work was completed, an article on the determination of silver in wines treated by this process has appeared (4).

Treatment of Raw Brandies

Raw apple brandy drawn directly from a commercial still was given the silver treatment by passage through the apparatus under a current strength of 0.8 milliampere and at a flow rate of 4 gallons (15 liters) per hour. A second sample was given a double passage through the apparatus at the same current strength, making an equivalent rate of 2 gallons (7.6 liters) per hour. These samples together with the control were placed in glass bottles and stored at room temperature for 6 days.

When these bottles were opened, the control sample of brandy had not changed in aroma or flavor, whereas both of the treated samples had a more mellow flavor and a pleasing aroma. It was apparent that the double treatment had accomplished the better artificial aging or mellowing in this product. Eleven months of storage in glass seemed to bring about very little change in any of these samples.

Chemical analyses were made on the raw and silver-treated apple brandy, and the results are recorded in Table I. These figures show that there was very little change in any of the flavoring constituents included in the analyses. There was, however, considerable change as far as the flavor and aroma were concerned; but apparently either this change was not represented in the constituents included in the analyses, or it was too slight to be detected by chemical means.

In the fortifying of wines it is customary to permit the fortified product to stand for a time to allow for the mellowing of the brandy flavor. It was thought that this period could be shortened by treating the fortifying brandy with silver before it was added to the wine.

Grape brandy (180 proof) was passed through the silvering apparatus under a current strength of 2.3 milliamperes at a rate of flow of 4.75 gallons (18 liters) per hour. After 5 days of storage in glass the treated product was pronounced superior to the control in both flavor and aroma. For tasting, these samples were diluted to 90 proof, since the higher proof made it impossible to taste the real flavor. There was very little change in the brandy as shown by chemical analysis (Table I).

TABLE I. EFFECT OF SILVER T	REATM	ENT ON	RAW B	RANDIES	
Sample	Acids as Acetic	Esters as Ethyl Acetate	Fusel Oil	Aldehydes	
	Tresseres.	Gram per 100 cc			
Raw apple brandy, 102 proof One treatment, 4 gal./hr. at 0.8 ma. Two treatments, 4 gal./hr. at 0.8 ma.	0.0369ª 0.0312 0.0300	$\begin{array}{c} 0.0303 \\ 0.0302 \\ 0.0295 \end{array}$	$0.0422 \\ 0.0408 \\ 0.0408$	0.0020ª 0.0015 0.0017	
Raw grape brandy, 180 proof One treatment, 4.75 gal./hr. at 2.3	0.0859	0.2063	0.2913	0.0150	
 a Analysis by Ada M. Smith. 	0.0778	0.2086	0.3124	0.0125	

Only a small quantity of each of the samples of grape brandy was available; but when a Tokay type wine was fortified with them, a mellowing effect was easily discerned in the silver-treated product.

Treatment of Quick-Aged Apple Brandy

In another series of experiments, samples of apple brandy were drawn from a commercial quick ager and subjected to the silver treatment. This brandy was light amber in color and possessed much more character and quality than a raw product.

A sample of the brandy was treated by passage through the silver apparatus at a rate of 4 gallons per hour under a current strength of 0.8 milliampere; another was passed through a second time, giving an equivalent rate of 2 gallons per hour. They were bottled and held at room temperature for 6 days and then opened for tasting. The hot, harsh flavor of the control sample had not changed; but in both of the treated samples the harshness had given way to a mellowness, and a pleasing aroma had developed. Samples were submitted to a number of persons, and in every case the treated samples were chosen as being superior to the untreated. The single silver treatment gave better results than the double passage through the apparatus. Eleven months of storage in glass did not seem to intensify the change in either flavor or aroma of any of the samples.

Chemical analyses were made on all of the samples and as can be seen from Table II, there were no significant changes in any of the determined constituents. The slight changes are well within the limits to be expected from experimental error.

TABLE II. EFFECT OF SII APP	LE BRAN		NT ON	QUICK-AGED
No. of Treatments at 4 Gal./Hr. and 0.8 Ma.	Acids as Acetic	Esters as Ethyl Acetate <i>Gram</i>	Fusel Oil per cc	Aldehydes
Untreated One Two ^a Analysis by Ada M. Smith.	$\begin{array}{c} 0.0369^{a} \\ 0.0312 \\ 0.0312 \\ \end{array}$	$\begin{array}{c} 0.0693 \\ 0.0700 \\ 0.0704 \end{array}$	$\begin{array}{c} 0.0932\\ 0.1020\\ 0.0936 \end{array}$	${}^{0.0060^a}_{0.0050}_{0.0045}$

Effect of Temperature on Silver Treatment

In order to test the possibility that temperature might influence the rate of reaction of the silver-aging process, samples of quick-aged apple brandy were treated and stored at different temperatures. The brandy used had been held in an oak barrel for a few days but had not taken on any of the "woody" taste.

TABLE III.	EFFECT OF	FREATMENT AN	D TEMPERATURE	ON CHEMICAL
(des	CONSTITUENT	s of Quick-Ag	ED APPLE BRAN	DY

Sample	-Treatment-		Treatment Storage		Acids as Acetic	Esters as Ethyl Acetate	Fusel Oil	Aldehydes
	Gal./hr.	Ma.	° C.	° C.		-Gram per	100 cc	
$\begin{array}{c}1\\2\\3\end{array}$	Control 4.4 4.4	sample 1.2 1.2	15 15	$\begin{array}{c} 0\\ 0\\ 25\end{array}$	$\begin{array}{c} 0.0300 \\ 0.0300 \\ 0.0312 \end{array}$	$0.0660 \\ 0.0625 \\ 0.0634$	$\begin{array}{c} 0.1109 \\ 0.1074 \\ 0.1105 \end{array}$	$0.0030 \\ 0.0030 \\ 0.0030 \\ 0.0030$
$\begin{array}{c} 4\\ 5\\ 6\end{array}$	Control 4.4 4.4	sample 1.2 1.2	15 15	37 37 45	$\begin{array}{c} 0.0336 \\ 0.0348 \\ 0.0270 \end{array}$	$0.0616 \\ 0.0625 \\ 0.0634$	$\begin{array}{c} 0.1091 \\ 0.1065 \\ 0.0942 \end{array}$	$0.0025 \\ 0.0020 \\ 0.0025$
7 8 9	Control 3.84 1.90	sample 1.2 1.2	$25 \\ 25 \\ 25$	25 25 25	$\begin{array}{c} 0.0312 \\ 0.0324 \\ 0.0354 \end{array}$	$0.0570 \\ 0.0542 \\ 0.0588$	$\begin{array}{c} 0.1041 \\ 0.1126 \\ 0.1109 \end{array}$	$\begin{array}{c} 0.0020 \\ 0.0025 \\ 0.0025 \end{array}$
$\begin{array}{c}10\\11\\12\end{array}$	Control 4.17 2.13	sample 1.3 1.3	$\dot{45}$ 45	$\begin{array}{c} 45\\ 45\\ 45\end{array}$	$\begin{array}{c} 0.0288 \\ 0.0282 \\ 0.0276 \end{array}$	$\begin{array}{c} 0.0651 \\ 0.0528 \\ 0.0572 \end{array}$	$\begin{array}{c} 0.0880 \\ 0.0950 \\ 0.0898 \end{array}$	$\begin{array}{c} 0.0025 \\ 0.0020 \\ 0.0020 \end{array}$

As shown in Table III, one set of samples was treated at 15° C. and stored at 0°, 25°, 37°, and 45° C.; another set was treated and held at 25° C.; still another was treated and stored at 45° C. All samples were stored at these temperatures for 20 days. Treatment at 15° and 25° C. gave similar results; treatment at 45° C. seemed to give an inferior product. This behavior might have been due to the fact that the brandy was heated to 45° C. in an open container; although the process took only a few minutes, some of the more volatile flavoring constituents might have escaped. This theory did not account for all of the loss of flavor, however, since brandy treated at 25° and held at 45° C. was not as good a product as those held at 0°, 25°, and 37° C. The chemical analyses (Table III) indicate that there were only slight differences in the various samples and that there seemed to be no indicated increase in flavoring constituents to correspond to the change in flavor. Material stored at 0° C. did not appear to respond to the treatment so rapidly as that held at higher temperatures but at the end of a week had reached its maximum change of flavor and aroma as against about 4 to 5 days when held at 25° or 37° C. Very little difference in flavor could be detected between samples held at 15°, 25°, and 37° C. It was estimated from these experiments that brandy could be treated at temperatures ranging from 15° to 37° C. and could be stored at temperatures from 0° to 37° C. without suffering deterioration in quality.

Treatment of Aged Apple Brandy

A commercial package of aged apple brandy which had been quick-aged and then stored in wood for 10 months before bottling for sale was subjected to the silver treatment. It was passed through the silver apparatus at a rate of flow of 4 gallons per hour under a current strength of 1.2 milliamperes. The treated and untreated materials were stored in glass for 4 days at room temperature before being opened. Upon examination the treated brandy was found to be superior to the untreated in both flavor and aroma. The samples were submitted to competent brandy tasters who had been in the brandy manufacturing business for years, and on a "blind " test the treated sample was chosen as being superior in aroma and flavor. These samples were also submitted to persons who had never smelled or tasted apple brandy, and they also chose the treated samples as being more pleasing and mellow than the untreated samples.

Effect of Storage on Silvered Brandies

All of the samples of brandy were stored 7 months in glass to see if any undesirable changes would take place because of the silver treatment. A small amount of sediment was deposited in all of the brandies which had been through the commercial quick ager or had stood in wooden containers. The silver-treated samples threw down more sediment than the untreated when held at 37° and 45° C., but about the same amount as the untreated samples when held at 0° and 25° C. It was thought that the deposition of this material might change the flavor, but no difference in either aroma or flavor could be detected except that the 45° C. series was inferior to the others. Certain of the silver-treated samples were filtered after the 7-month storage and bottled. These filtered samples were held at room temperature for about 11 months, and no sediment could be detected in the product. The flavor remained unchanged in all of the samples.

Summary

When raw, quick-aged, and naturally aged brandies were passed through a small laboratory device, the products became mellowed within 5 days and considerable change in flavor and aroma had developed. Additional storage in glass failed to show a greater aging effect on either the aroma or flavor.

Brandy was silver-treated at 15° , 25° , and 45° C. The 45° C. treatment gave poor results, while little difference was noted between the 15° and 25° C. treatments. Samples of the various treatments were stored at 0° , 25° , 37° , and 45° C.; satisfactory results were noted at the first three temperatures but not at 45° C.

Grape brandy used for fortifying wine was silver-treated, and a mellowing effect was noted. When used for fortifying purposes, there was a discernible difference between the treated and untreated samples.

Chemical determinations were made on both treated and untreated samples for acids, esters, aldehydes, and fusel oil. In no case could a significant change in these constituents be noted as a result of the silver treatment, although there was a pronounced difference in the flavor and aroma. It is possible, either that the particular components responsible for the flavor change were not members of the group of compounds under observation, or that the change, while discernible to the taste, was so slight that it could not be detected by the chemical methods employed.

Sediment was deposited in greater amount in the treated samples than in the untreated, but when the treated brandy was filtered and held in glass, no more sediment appeared.

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