STUDIES WITH BRANDY. II. TANNIN

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It is commonly assumed that there is an increase in the tannin content of brandies during aging although there is very little analytical data on the subject. Newly distilled spirits contain no coloring matter or tannin. During aging both are dissolved from the wood. The tannins extracted from various types of wood differ in their properties, those from oak being the most desirable for the aging of brandy. Oak from different locations is considered to be of varying degrees of desirability, and producers of high-quality brandy have marked preferences for containers made of oak from particular localities.

According to Russell (1935) the chief natural tannin occurring in oak wood is a phlobatannin. Phlobatannins are phlobaphene-producing tannins and phlobaphenes are red or brown, amorphous, insoluble materials which are most easily produced from the phlobatannins by heating with dilute mineral acids. The fission products of oak-wood tannin obtained by Russell were phloroglucinol and gallic acid. Freudenberg and Vollbrecht (1922), however, by means of tannase hydrolysis, obtained five per cent glucose, 23 to 25 per cent ellagic acid and amorphous quercusic acid. Kurmeier (1927) found ellagic acid but no sugar. Others have reported protocatechuic acid and catechin as oak-wood tannin fission products. This confused picture led Gisvold and Rogers (1939) to consider oak tannin as an unclassified tannin rather than a phlobatannin. (The confusion may be more apparent than real owing to the varying types and ages of oak wood which have been analyzed by various investigators.)

Whatever the exact constitution of oak tannin, it is chemically related more or less closely to catechin, and one of the fission products frequently reported from catechin as well as from oak tannins is protocatechuic acid. Vanillin is the methyl ether of protocatechuic acid.

Reif (1927) has reported the presence of 0 to .2 mg. of vanillin per liter of spirits. The vanillin he believed to have been extracted from the wood, and the amount found was roughly proportional to the brown color of the spirits. A perceptible vanillin-like odor is observed when brandy is first removed from a new oak barrel after aging for three or four years. Only very minute amounts of vanillin are necessary to give a detectable odor. Watts (1939) states that 2×10^{-10} mg. of vanillin per liter of air can be detected. There is a possibility that young red wines may contain vanillin and that it would be distilled. Seifert (1938) reports that Mach found vanillin in grape seeds and that red wines, which are fermented on the seeds, had a perceptible vanillin odor.

In general, it is known that the smaller the cooperage the more rapid the coloration and the faster the extraction of tannin. Probably this is because of the greater surface-to-volume ratio in the smaller containers and also because of the greater percentage loss of liquid from small containers and resulting concentration of the nonvolatile constituents remaining. The longer the aging the greater the tannin content. Used cooperage obviously contains less extractable tannin material.

Joslyn [Joslyn and Amerine (1941)] made experiments on the effect of treatment of the cooperage on the tannin content. After one year of aging in 50-gallon barrels he found that brandy stored in barrels which had been treated with sodium hypochlorite, soda ash, or which had been steamed, paraffined, or charred before use, had a smaller tannin content compared with brandy stored in untreated new white oak containers. Addition of two ounces of quercyl seemed to increase the extracted tannin by the method of analysis used. Except for the marked reduction in tannin content after hypochlorite or soda ash treatments, the results were somewhat variable.

Valaer (1941) reported that the tannin content increases with age and that rapid-aging procedures involving the use of oak chips increases the tannin content disproportionately to the other constituents. He reports 22 mg. of tannin per 100 ml. in a brandy sample and 32 mg. in whisky. These figures may not be exact, since his reaction time did not exceed 15 minutes. Rosenblatt and Peluso (1941) found 22.7, 60.1, and 72.7 mg. per 100 ml. in three whiskies.

When brandies that have been stored in new oak cooperage are reduced in proof from 103° to 88°, a reddish precipitation frequently occurs. A portion of this precipitate is apparently due to the fact that caramel syrup becomes less soluble. Phlobaphene precipitation, however may also be partially responsible. Yasin (1938) has shown that extracts made from freshly cut oak settle slowly and are difficult to filter, while extracts from dry oak settle well and filter easily. The time of sedimentation, therefore, appears to be directly proportional to the moisture content of the wood and inversely proportional to the age of the wood. Improperly seasoned new oak has often been used for brandy in California. The tannin extracted from some of it is probably a cause of sediment in certain brandies.

EXPERIMENTAL PROCEDURE AND RESULTS

The tentative procedure of the Association of Official Agricultural Chemists, as proposed by Valaer (1941), was used for the determination of tannin except that the solutions were allowed to stand one hour before making any readings, as recommended by Rosenblatt and Peluso (1941). This method depends on the reactivity of the Folin-Denis reagent (made of sodium tungstate, phosphomolybdic, and phosphoric acids) for oxyphenyl compounds and is therefore not specific for tannins. Interfering substances are present only in small amounts in brandy. The tannic acid used contained eight per cent moisture and this was taken into account in the calculations.

An attempt was also made to measure the vanillin content. Reif's procedure (1927) was tried but only qualitative data could be obtained. A number of colorimetric procedures were investigated, but in all cases the same color or a similar color could be produced by tannin. Such colorimetric tests as bromine and ferrous sulfate, resorcinol, phloroglucinol, or ferric chloride all failed. Reif's sublimation procedure was also tried.

Small quantities of vanillin seem to be detected by this latter method, but quantitative data are difficult to obtain. It is concluded that if vanillin is present, it occurs only in very small amounts.

The color of the brandies was determined by the method previously reported by Tolbert and Amerine (1942). The standard contained 1.1, 1.0, and .2 ml. of one-half per cent solutions of red, yellow, and blue Eastman ABC dyes per 100 ml.

The brandies used for tannin determination are the same as those reported in the previous article by Guymon, Tolbert, and Amerine (1943).

The tannin and furfural content of the Exposition brandies are given (Table 1); the considerable variation in tannin content between the samples indicated that they had been aged for different periods of time or that oak chips had been used. We have been advised that this was the case for the two brandies containing the largest amount of tannin. In general the high tannin samples had high furfural, extract, and total acid.

TABLE 1

Tannin, Furfural, Total Acid, and Extract Content of Exposition Brandies

No.	Tannin	Furfural	Total acid	Extract
	mg./100 ml.	*mg./100 ml.*	*mg./100 ml.*	*mg./100 ml.*
A	10.2	0.27	.0322	.0984
B	9.3	0.24	.0276	.0968
C	17.0	1.04	.0480	.1306
D	49.2	1.89	.0575	.2342
E	3.0	0.94	.0390	.0266
F	10.0	0.19	.0193	.0740
G	10.6	0.43	.0257	.1294
H	47.5	1.00	.0515	.1820
I	20.5	1.02	.0658	.1486
J	16.5	0.79	.0377	.1410

No relationship between the amount of tannin and the ester, fusel oil, aldehyde, acetal, copper, or ash content was observed.

The Prorate brandies were newly distilled and very recently barreled when the samples were taken. Very little tannin could therefore be found, only a trace to 2.0 mg. per 100 ml., averaging only 1.0. This is probably not all tannin, small amounts of other substances reacting with the Folin-Denis reagent being present.

The pertinent analytical data on the University brandies are given (Table 2); the data have also been recalculated on the basis of the amount of tannin per 100 ml. of original brandy present. The tannin and color content increase with age, are greater in small than in large cooperage, and do not appear to be affected by moderate pretreatment of the cooperage except after actual brandy storage or after charring and scraping. There is a very marked reduction in color and tannin extraction in these two latter cases. In the 50-gallon barrel there was about 30 mg. of tannin per 100 ml. after two years of aging.

Although there is a regular progression in tannin content in the barrels of different sizes after one year of storage, the 50-gallon container is inconsistent in the second and third year. When this container is finally

TABLE 2

Tannin and Color Content of University Brandies in Various Types of Containers

University No.	Number of containers	Barrel size[1]	Barrel treatment[2]	Tannin: To original volume 1941[3]	Tannin: To original volume 1942	Tannin: To final volume 1941	Tannin: To final volume 1942	Color 1941	Color 1942
1939 Brandies									
				mg./100 ml.	*mg./100 ml.*	*mg./100 ml.*	*mg./100 ml.*		
17	1	5	Rinsed with brandy	32.0	33.6	38.0	51.5	73	87
18	1	10	Rinsed with brandy	28.7	30.2	32.6	41.7	39	51
19	1	15	Rinsed with brandy	23.1	26.6	25.2	32.8	36	48
20	1	25	Rinsed with brandy	23.8	26.4	25.4	30.8	40	52
21	1	50	Rinsed with brandy	22.6	28.6	23.5	32.1	52	73
22	1	50	Charred; scraped out; rinsed with brandy	6.7	9.6	7.1	11.0	12	16
23	1	25	Two-year-old brandy barrel	7.3	11.2	8.1	13.7	22	30
27	1	5	Na_2CO_3 wash; soaked with brandy	36.2	38.0	41.7	56.2	64	83
....	19	5	Rinsed with brandy	37.1	38.5	44.0	57.5	66	80
....	3	5	Steamed; soaked with brandy	33.5	36.8	39.4	56.7	65	81
1940 Brandies									
78	1	25	Steamed; soaked with brandy	13.2	19.3	14.9	24.0	30	53
79	1	25	Old brandy barrel	5.4	10.9	5.9	13.4	14	25
....	22	5	Boiled hot water; soaked with brandy	33.6	37.5	38.3	55.8	75	122
....	29	10	Boiled hot water; soaked with brandy	20.0	26.0	22.6	35.0	32	55

[1] In gallons. [2] All barrels were new unless otherwise stated. [3] Actual dates of withdrawal of samples: 1939 brandies were put in barrels Dec. 22, 1939, to Jan. 16, 1940; 1941 analyses were drawn Jan. 15, 1941; 1942 analyses on Jan. 19, 1942; 1940 brandies were put in barrels Oct. 23, 1940, to Jan. 16, 1941; 1941 analyses were drawn Aug. 4, 1941; and 1942 analyses on Aug. 8, 1942.

emptied it will be possible to examine the inner surfaces of the staves to determine if any faults were present which could account for the greater color and tannin extraction.

DISCUSSION

The amounts of tannin present in California brandies are decidedly variable. This is one of the reasons for the dissimilarity of many of the commercial brandies. The differences arise from the use of new oak *versus* used cooperage, from differences in temperature and period of storage, and from the use by some producers of oak chips or tannin extracts. The presence of too much tannin in brandy is also reflected in too dark a color. These dark brandies have an astringent or harsh taste which is undesirable. The tannin content may be readily reduced by the use of certain types of activated charcoal, according to Tolbert and Amerine (1942).

TABLE 3

Tannin Extracted From Oak Barrels[1] per Square Sentimeter of Exposed Surface per Year

University No.	Approximate barrel size	Area [2]	Tannin extracted [3]		
			1941	1942	Total
	gal.	*cm.*^{2}	*mg./cm.*^{2}	*mg./cm.*^{2}	*mg./cm.*^{2}
17	5	3,965	1.47	.08	1.55
18	10	6,200	1.69	.09	1.78
19	15	9,100	1.45	.20	1.65
20	25	12,200	1.86	.20	2.06
21	50	18,440	2.22	.59	2.81

[1] New barrels were rinsed with brandy only before use. [2] Area equals:

$$\frac{\pi}{2}\left[\sqrt{(b^2-d^2)+h^2d^2}+\frac{h^2b^2}{\sqrt{(b^2-d^2)(h^2+d^2-b^2)}}\ \sin^{-1}\ \frac{\sqrt{(b^2-d^2)(h^2+d^2-b^2)}}{bh}\right]+\frac{\pi}{2}d^2$$

where h = depth, b = diameter at center, d = diameter at the top and bottom (all inside measurements). The authors are indebted to Professor E. B. Roessler for this formula. [3] Calculated to the original volume of the brandy.

The increase in tannin during aging occurs in much the same fashion as in whisky, although the amounts found in brandy are somewhat greater. The amounts extracted per square centimeter of exposed surface per year in containers of different sizes are given (Table 3).

The amount of tannin extracted by brandies contained in small cooperage is much greater in concentration than by those contained in large cooperage (Table 2). However, it appears from Table 3 that there is a lesser degree of extraction of the total tannin from the wood by brandies stored in small cooperage. This may be due to the fact that the smaller containers have a smaller percentage of their available surface in contact with the brandy after one or two years of aging. But as more total tannin is extracted after the first year of aging from the largest barrel, the extraction must be more dependent upon the concentration of tannin and solids in the brandy. In agreement with this the rate of tannin extraction is greatest during the first year.

The rate of extraction of tannin by brandies is therefore assumed to be limited by the concentration of tannin, and possibly of other soluble material in the brandy. The total tannin extracted from the five- and 10-gallon barrels after two years of aging is only about one-third as much as in the 15- and 25-gallon containers. The only other apparent explanation is that the tannin has been removed from the staves of the smaller containers; but Table 3 indicates that this is not the case, since more tannin is extracted per square centimeter from the large containers which are made from the same type and age of wood.

The color differences are roughly the same as the tannin differences. Crampton and Tolman (1908) found a gradual darkening of whiskey. Valaer (1941), however, in his studies on the aging of brandy did not find a very regular increase in color.

SUMMARY

The tannin content of commercial, newly distilled, and experimental brandies has been determined. Commercial brandies contain from three to 47.5 mg. of tannin per 100 ml., averaging 19.3 mg. Newly distilled cut and colored brandies contain only about one mg. per 100 ml. of tannin as determined with the Folin-Denis reagent. The tannin, furfural, total acid, extract, and color contents increase more or less at the same rate. Brandy stored in small cooperage contains more tannin than that stored in large cooperage. This is true even if the losses owing to evaporation are taken into account. However, more tannin is extracted per square centimeter of surface from larger barrels. The concentration of tannins and other solids in the brandy is apparently the limiting factor for the amount of tannin extracted from the barrel. Very little vanillin could be found in California brandy.

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