Influence of Aging Factors on the Furanic Aldehyde Contents of Matured Brandies: Aging Markers

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Appropriate statistical techniques were used to study the influence of different aging conditions on the furanic aldehyde contents of a number of brandies. Some of these conditions (presence or absence of caramel, wood type, state of the barrel, length of maturation) affected the concentrations of furfural and 5-(hydroxymethyl)furfural in the distillate, and these compounds cannot therefore be taken as aging markers.

Keywords: *Furfural; 5-(hydroxymethyl)furfural; brandies; aging markers*

INTRODUCTION

Several authors have used **furfural** content as an **approximate indicator** of the **authenticity** and **age** of brandies and other alcoholic beverages stored in oak barrels. Thus, López Gonzalez (1964) found that furfural is a standard component in spirits aged in wood, and so its determination is significant in cataloging authentic beverages. López Gonzalez determined this aldehyde in all commercial bottled brandies and found the maximum values to correspond to the highest quality brandies. For whiskeys, the results from authentic samples subjected to aging were much higher than those from other suspect products. If the beverage was prepared by simple dilution of rectified alcohol with addition of flavoring and coloring, the furfural content was low or nonexistent.

Similarly, studies undertaken by Johnson (1969) on maturing whiskey showed that color, acids, esters, tannins, and furfural increased during maturation. Bozhinov and Bekalov (1983) considered the furfural content, together with total sugars and total phenols, to be a good **age marker**, since the concentrations of these compounds increase with time on addition of oakwood extracts to the brandy samples analyzed.

This can lead us to consider furfural as a possible indicator of maturation in wood. Marsal and Sarre (1987) found satisfactory levels of furfural in wines kept in barrels for a certain length of time, whereas the same wines stored in steel vats contained none. Likewise, Moutounet et al. (1989) referred to the increase of furfural and 5-(hydroxymethyl)furfural in spirits aged in oak barrels; these furanic aldehydes are extracted from the wood of the barrel by the spirit, so the presence of furfural and 5-(hydroxymethyl)furfural can be taken as an aging marker.

However, not all authors consider these substances suitable aging markers for spirits. Onishi et al. (1977) stated that the extraction of furanic aldehydes depends not only on how long the spirit was in the barrel but also on other factors such as the type of oak used for the barrel, barrel size, and barrel age. These authors found that spirits aged in American oak barrels presented higher furfural and 5-(hydroxymethyl)furfural contents than the same spirits aged in French oak barrels, although the latter seem to contribute more to the color of the brandy than American oak.

Jeuring and Kuppers (1980) reached similar conclusions. They found that part of the furfural present in brandy originated in the distillation process, so that the presence of this furanic aldehyde in a spirit cannot be taken as an indicator or marker of aging.

Finally, Profumo et al. (1988) also expressed doubts about the use of furfural as an age marker: "a glance at the furfural concentrations found in the samples allows us to affirm the nonutility of this parameter for evaluation of the length of maturation of the distillate, as there are no appreciable differences between recent distillates and the samples aged in oak." If we also take into account that most of the 5-(hydroxymethyl)furfural found in the samples of bottled brandy is the result of the addition of caramel coloring (Pons et al., 1991), this compound can hardly be taken as a possible aging marker either (Puech et al., 1988).

The aim of this paper is to use suitable statistical techniques to determine the influence on the furanic aldehyde contents in matured spirits of the different factors affecting aging conditions, i.e., presence of caramel, aging technique, wood used for maturing, state of the barrel, and duration of aging. To this end we analyzed the furfural and 5-(hydroxymethyl)furfural contents in samples of commercial brandies and wine spirits aged according to different techniques and in different types of oak barrels.

MATERIALS AND METHODS

A. Samples Analyzed. The samples analyzed included 72 samples of commercial brandy containing caramel and 46 samples of brandy without caramel coloring, the aging of which was constantly controlled. According to their characteristics, these samples were classified as follows: *according to the aging method* (26 samples of brandy aged by the traditional method, 20 samples of brandy aged by the soleras method); *according to the type of wood used for the barrel* (22 samples of brandy aged in French oak barrels); 20 samples of brandy aged in American oak barrels); *according to the conditions and usage of the barrel* (16 samples of brandy aged in new barrels with charred staves, 18 samples of brandy aged in barrels used for other products for 5 years, 12 samples of brandy aged in new barrels with unburnt staves); *according to maturation time* (7 samples of unaged brandy, 7 samples of brandy aged for 12 months, 8 samples of brandy aged for 24 months, 8 samples

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Table 1. Characteristics of the Variables Studied

series	level	sample size	KW av rank (mg/L)
furfural/caramel	with caramel	72	47.7500
	without caramel	46	77.8913
5-HMF/caramel	with caramel	72	82.3472
	without caramel	46	23.7391
furfural/aging style	traditional	26	23.5125
	soleras	20	23.4167
5-HMF/aging style	traditional	26	24.6500
	soleras	20	15.8333
furfural/wood type	French oak	22	23.3182
	American oak	24	23.6667
5-HMF/wood type	French oak	22	25.3864
	American oak	24	21.7708
furfural/barrel condition	new and burnt	16	33.5000
	used	18	21.2222
	new	12	09.9167
5-HMF/barrel condition	new and burnt	16	32.9167
	used	18	18.8611
	new	12	14.0417
furfural/time (months)	0	7	13.5000
	12	7	24.0714
	24	8	22.6429
	36	8	20.6429
	48	8	23.8571
	60	8	24.2857
5-HMF/time (months)	0	7	10.0000
	12	7	17.2857
	24	8	20.9286
	36	8	24.2857
	48	8	27.0000
	60	8	29.5000

of brandy aged for 36 months, 8 samples of brandy aged for 48 months, 8 samples of brandy aged for 60 months).

B. Chromatographic Method. Determination of the furanic aldehydes in the foregoing samples was carried out by high-performance liquid chromatography, following the technique developed by Villalón Mir et al. (1992). The results obtained were subjected to statistical analysis using the Statgraphics v. 5.0 program.

RESULTS AND DISCUSSION

The furfural and 5-(hydroxymethyl)furfural contents were examined with regard to the following variables or aging factors: (1) presence or absence of caramel in the brandies; (2) type of aging used in maturing the samples (traditional or soleras); (3) type of wood used for the barrels (French or American oak); (4) conditions of the barrels (new and burnt, used for other products for 5 years, and new, unburnt barrels, specially made to age the spirits studied here); (5) aging time, measured in months.

Table 1 shows the characteristics of the variables (or aging factors) studied here. The furanic aldehyde concentrations in the samples were subjected to the Kruskal−Wallis (KW) or ANOVA I tests to determine whether the variations in concentration were due to the genuine influence of aging factors or had occurred purely by chance.

The results were previously subjected to Kolgomorov−Smirnov (KS) and Bartlett tests to examine whether the different sample populations had normal distribution and homogeneity of variances. If this was the case, we then applied the ANOVA I test, whereas abnormal distribution and/or heterogeneity of variances led to application of Kruskal−Wallis rank analysis.

Furfural/Caramel. We first examined the furfural/caramel variables. The KS test showed differences between normal distribution and that of our samples. This population does NOT therefore follow a normal (or Gaussian) distribution. The Bartlett test for homogeneity of variances was equally significant, as it revealed considerable differences in the variances of the samples.

It was therefore necessary to apply the nonparametric KW test, which demonstrated the influence of the presence of caramel on the furfural contents found in the samples. A significance level lower than 0.01, which is the level required by this test, showed the influence of caramel on the furfural contents (Table 2).

5-(Hydroxymethyl)furfural/Caramel. The KS test returned results lower than the 0.05 significance level required to consider normal distribution of the samples examined. The Bartlett test gave results lower than 0.05, so there are also significant differences in the variances. Subsequent application of the KW test gave a significance level of 0 for 5-(hydroxymethyl)furfural on caramel. This therefore indicates the considerable influence of caramel on the presence of 5-(hydroxymethyl)furfural in the samples of aged brandies (Table 2). This result was expected, in view of the results obtained in the study of furanic aldehyde concentrations in commercial caramels (Villalón Mir et al., 1992), where the most abundant furanic component was 5-(hydroxymethyl)furfural (234.9 compared with 2.1 mg/kg of furfural).

Furfural/Aging. As the influence of caramel on the presence of furfural and 5-(hydroxymethyl)furfural in aged brandy samples has been indicated above, in the remaining studies we only examine those samples which we know not to contain caramel. We thus avoid anomalous results in the furanic aldehyde concentrations detected in the samples resulting from the amounts of these two compounds contributed by caramel.

In this case, the KS test judging the degree of fit for normal distribution gave results identical to those previously obtained, with a significance level lower than 0.05, which indicates the abnormal distribution of the corresponding sample population. The Bartlett test for homogeneity of variances also showed a confidence level lower than the 0.05 required as a minimum for this test, indicating significant differences in the variances.

The KW test was therefore applied to determine the influence of the different types of aging on the furfural content of the matured brandies. The results show that there are no significant differences in the furfural concentrations of the brandies aged by either method. We therefore take it to be proven that the different aging methods have no influence on the furfural contents of the brandies (Table 2).

5-(Hydroxymethyl)furfural/Aging. The sample population studied in this case is also affected by abnormal distribution, which, together with the fact that the variances show poor homogeneity, leads once more to application of the nonparametric KW test.

In this case, we obtained a significance level higher than the 0.01 required, and so there are no statistically significant differences in the 5-(hydroxymethyl)furfural concentrations found in the brandy samples aged according to the different methods. We can therefore state that the aging technique has no influence on the presence of 5-(hydroxymethyl)furfural in the brandies (Table 2).

Table 2. Influence of the Different Aging Variables on the Furanic Aldehyde Contents of the Samples of Matured Brandies

series	KS test	Bartlett test	test	statistics test	sig level KW test
furfural/caramel	3.0*E*−5 (S)[a]	2.18*E*−3 (S)	KW	21.8026	3.02*E*−6 (S)
5-HMF[c]/caramel	3.6*E*−5 (S)	0 (S)	KW	82.7356	0 (S)
furfural/aging style	5.22*E*−4 (S)	8.77*E*−5 (S)	KW	2.67*E*−4	0.99 (NS)[b]
5-HMF/aging style	2.91*E*−3 (S)	6.58*E*−5 (S)	KW	2.42	0.12 (NS)
furfural/wood type	5.22*E*−4 (S)	2.39*E*−3 (S)	KW	7.77	0.93 (NS)
5-HMF/wood type	2.91*E*−3 (S)	8.98*E*−4 (S)	KW	0.90	0.34 (NS)
furfural/barre condition	5.22*E*−4 (S)	3.26*E*−14 (S)	KW	22.35	1.41*E*−5 (S)
5-HMF/barrel condition	2.91*E*−3 (S)	1.24*E*−7 (S)	KW	17.26	1.79*E*−4 (S)
furfural/time (months)	5.22*E*−4 (S)	0.99 (NS)	KW	4.03	0.55 (NS)
5-HMF/time (months)	2.91*E*−3 (S)	0.99 (NS)	KW	12.93	0.024 (NS)

[a] (S), significant. [b] (NS), nonsignificant. [c] 5-HMF, 5-(hydroxymethyl)furfural.

Table 3. Aging Conditions Required for Furanic Aldehydes To Be Considered Aging Markers

furanic aldehyde/aging marker	condition required by aging marker	results obtained
furfural/caramel	no influence of caramel (NS)[a]	influence of caramel (S)[b]
5-HMF/caramel	no influence of caramel (NS)	influence of caramel (S)
furfural/aging style	no influence of aging (NS)	no influence of aging (NS)
5-HMF/aging style	no influence of aging (NS)	no influence of aging (NS)
furfural/wood type	no influence of wood (NS)	no influence of wood (NS)
5-HMF/wood type	no influence of wood (NS)	no influence of wood (NS)
furfural/barrel condition	no influence of barrel (NS)	influence of barrel (S)
5-HMF/barrel condition	no influence of barrel (NS)	influence of barrel (S)
furfural/time (months)	influence of aging time (S)	no influence of aging time (NS)
5-HMF/time (months)	influence of aging time (S)	no influence of aging time (NS)

[a] (NS), nonsignificant. [b] (S), significant.

Furfural/Wood. The significance level obtained by the KS test in this case was 0.000522, i.e., much lower than the 0.05 required. The sample population does not therefore have normal distribution. The Bartlett test also gave significance levels lower than 0.05, and so we were again forced to apply the KW test, with a result of 0.93, which indicates the absence of significant differences in the furfural concentrations detected in the brandies aged in the different types of oak. There is, therefore, no influence of the type of wood on the furfural content (Table 2).

5-(Hydroxymethyl)furfural/Wood. Once again, the distribution of our samples is not normal, with a significance level of 0.00291, and the Bartlett test reveals significant differences in the variances of the samples studied.

However, the KW test shows that there are no significant differences in the 5-(hydroxymethyl)furfural contents found in the samples aged in either wood (Table 2).

Furfural/Barrel. The nonparametric KW test was again used, in view of the abnormal distribution of the sample population according to the KS test and the variability of the variances.

The significance level obtained by the KW test showed the influence of the state of the barrel on the furfural content of the brandies aged in any of the barrels (Table 2).

5-(Hydroxymethyl)furfural/Barrel. The KS test again showed abnormal distribution and the Bartlett test significant differences between the sample variances.

The KW test (Table 2) indicates significant differences in the concentrations of 5-(hydroxymethyl)furfural found in each type of barrel examined. The state of the barrel therefore affects the 5-(hydroxymethyl)furfural contents of the samples.

Furfural/Months. The significance level of the fit to normal distribution was 0.000522, which indicates abnormal distribution of the samples. However, in this case, the Bartlett test gave a significance level higher than that required for the test, and so there are no significant differences in the variances of our samples.

Nonetheless, since application of a parametric test such as ANOVA requires the results of both the KS and Bartlett tests to be nonsignificant, we once more had to apply the KW test (Table 2), which revealed the absence of significant differences in furfural contents according to the different aging periods studied.

In view of these results, we can state that the length of the aging process does not affect the furfural concentrations in the samples analyzed.

5-(Hydroxymethyl)furfural/Months. The sample population in this case does not present normal distribution, as the KS test gave a significance level lower than 0.05. On the other hand, the Bartlett test showed a significance level higher than 0.05, which indicates homogeneity in the sample variances.

The situation was the same as in the preceding case, and again we were obliged to apply the KW test, which gave a significance level higher than 0.01, thus confirming the absence of significant statistical differences in the 5-(hydroxymethyl)furfural contents of the samples aged for different lengths of time (Table 2).

Table 3 shows the conditions that the different aging factors must fulfill for furfural and 5-(hydroxymethyl)-furfural to be considered age markers. Also shown are the results found in our samples in comparison with those necessary to consider these compounds as markers. It can be seen that factors such as the presence of caramel, the state and use of the barrel, and length of aging affect the furanic aldehyde concentrations found in matured brandies, whereas other factors, such as aging technique and the type of wood, do not seem to affect the furanic aldehyde concentrations.

In view of these results, furanic aldehydes cannot be considered aging markers of matured brandies, because of the influence on their concentrations of factors such as barrel exhaustion, the techniques used in barrel construction (burning or not of barrel staves), and the presence of caramel, as well as the lack of influence of the time factor on furfural and 5-(hydroxymethyl)-furfural contents. We must therefore look for other parameters not affected by aging conditions that can give an approximate indication of the age of a matured wine spirit, as we can never know with certainty the different aging variables to which a spirit is subjected.

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