Food Chemistry, Vol. 56, No. 4, pp. 415–419, 1996

0308-8146/96 $15.00+.00
0308-8146(95)00210-3

The influence of added caramel on furanic aldehyde content of matured brandies

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(Received 9 June 1995; accepted 2 October 1995)

A study was carried out on the furanic aldehyde content of commercial brandies and wine distillates subjected to controlled ageing, in order to determine the influence of caramel colour on the furfural/5-hydroxymethylfurfural ratio of these brandies. Use of suitable techniques established the influence of caramel colour on this ratio. Copyright © 1996 Elsevier Science Ltd

INTRODUCTION

Two furanic aldehydes, furfural and 5-hydroxymethylfurfural (5-HMF), are frequently found in a large number of foods. The origin of these compounds in foodstuffs is due, in some cases, to Maillard browning reactions or to the caramelization processes that take place when sugars are heated above their melting point (Cheftel & Cheftel, 1980; Badui Dergal, 1981; Ferenç, 1985).

However, for the purposes of this study, the origin we are most interested in is the one causing a significant presence of these furanic aldehydes in aged wine distillates, namely the thermolysis of polysaccharides found in the wood during the charring of oak barrels (Puech & Moutounet, 1988).

Among other substances, the chemical composition of wood includes lignin and polysaccharides such as cellulose and hemicellulose. When an oak barrel is made, the inner part of the staves is burnt and wetted to avoid breakage (Artajona Serrano, 1991). This treatment results in partial reduction of the cellulose, thus generating 5-HMF (Fengel & Wegener, 1984).

Furfural does not occur as such in oak wood, but is formed, as in the case of 5-HMF, by the thermolysis to which staves are submitted during charring. Furfural originates in the constitutive pentoses of the hemicellulose in oak wood. When the wood is burnt, thermolysis of the hemicellulose begins and, when the temperature reaches 200°C, the glycosidic and C–C links of the pyranose rings are broken. If the temperature rises to 225°C, molecular destruction begins, and at 290°C molecular fragments are dehydrated giving rise to furfural (Puech *et al.*, 1988).

The addition of caramel colour is another possible source of furanic aldehydes in brandies. This method is quite common in the elaboration of spirit beverages submitted to an ageing process and gives them an amber colouration that is attractive to the consumer (López Gonzalez, 1964; Puech & Moutounet, 1988).

The chemical composition of caramel is complex, due to the large number of substances produced as a result of pyrolysis in carbohydrates such as sucrose, glucose or starch. We must also take into account the presence of furanic compounds such as furfural or 5-HMF, of which the latter is found in much higher concentrations (Badui Dergal, 1981).

The aim of this study was to determine the furanic aldehyde contents of commercial brandies and wine distillates that had been subjected to controlled ageing. The use of adequate techniques should establish, not only the influence of caramel colour on furfural and 5-HMF concentrations, but, in particular, its influence on the ratio of these furanic compounds.

MATERIALS AND METHODS

Thirty-eight samples of commercial brandies were analysed, divided into two groups according to the ageing process involved: (1) commercial brandies aged by the dynamic system; (2) commercial brandies aged by the traditional static system.

Macerated mixtures of wood shavings in wine distillates were used to simulate the dissolution conditions of the compounds extracted by wine distillates from wooden barrels. The shavings were previously submitted to a charring process to simulate the heating undergone by the barrel staves during thermolysis. We also made a study of the most favourable conditions for maceration.

Analyses were carried out on two series of macerated mixtures, one containing French oak shavings and the other American oak shavings. Both series were subjected

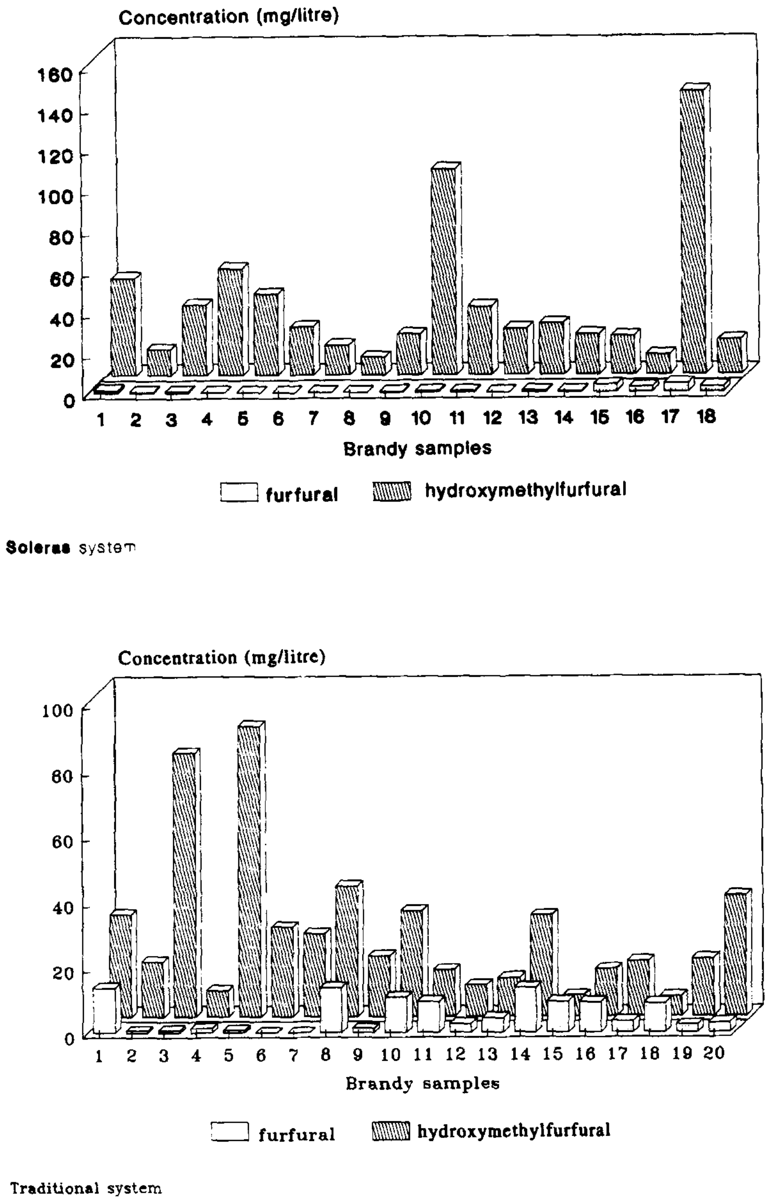


Fig. 1. Furanic aldehyde concentrations found in the samples of commercial brandies.

to a static maceration process for a period of 2 years. Caramel was not added to these samples.

The analytical technique used was high-perfomance liquid chromatography with direct injection of the samples previously filtered through 0.45 μm Millipore membranes (Villalón Mir *et al.*, 1992).

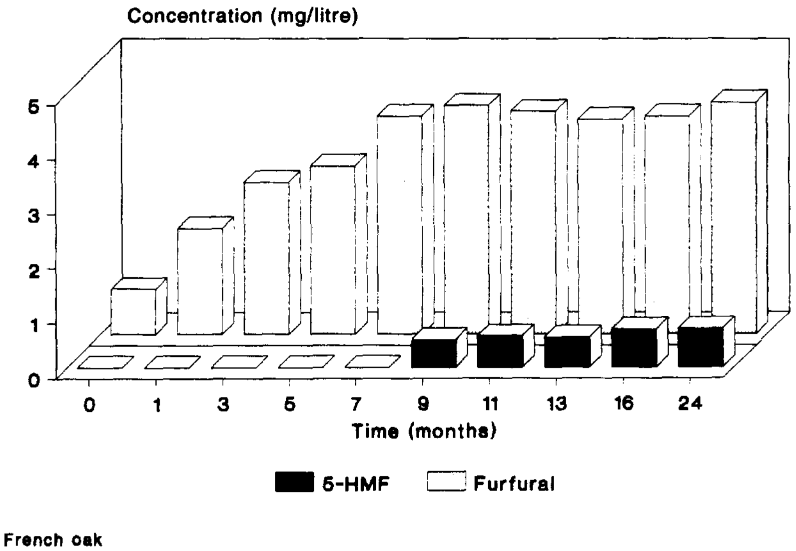
We likewise applied the technique accepted by the Association of Official Analytical Chemists (AOAC, 1990) for qualitative determination of caramel colour in wines and wine distillates, as well as statistical analysis by the Kolmogorov–Smirnov and one-way analysis of variance (ANOVA) tests, using the STATGRAPHICS v5.0 package (Statgraphics, 1991).

RESULTS AND DISCUSSION

The concentrations of furanic aldehydes in both types of samples analysed are represented in Figs 1 and 2. The furfural/5-HMF ratios were obtained using these concentrations.

Almost all the furfural concentrations found in these samples (0.99 mg litre^{-1} average concentration in commercial brandies aged by the dynamic system, and 5.83 mg litre^{-1} in those aged by the traditional system) are lower than the 5-HMF concentrations (35.66 mg litre^{-1} and 26.5 mg litre^{-1}, respectively). The furfural/5-HMF ratios are less than 1 in all the samples, except for two samples in the traditional series where the ratio is higher than 1 (1.4 and 1.50). The ratios in both series vary from 0 to 0.663.

However, for the macerated mixtures of French and American oaks (Fig. 2), to which caramel had not been added, the furfural concentrations are always higher than those of 5-HMF (average 3.32 mg litre^{-1} for furfural and 0.3 mg litre^{-1} for 5-HMF in French oak, and 2.04 mg litre^{-1} for furfural and 1.10 mg litre^{-1} for 5-HMF in American oak). The furfural/5-HMF ratios



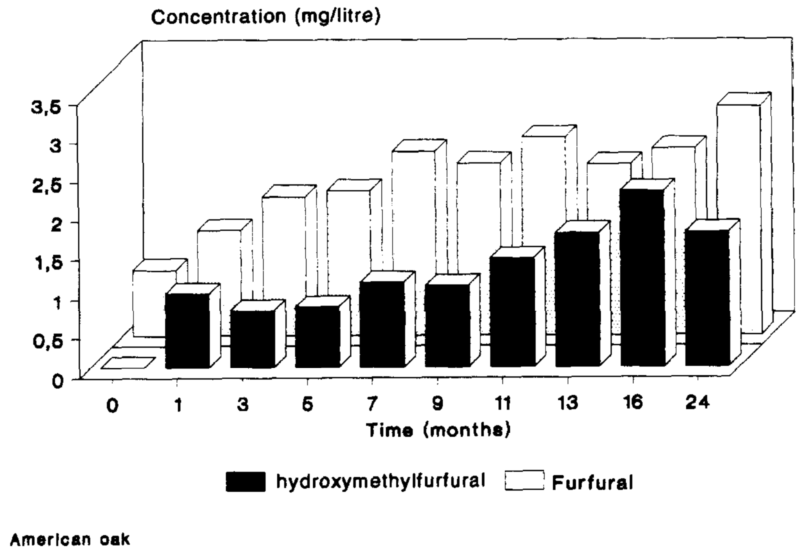


Fig. 2. Furanic aldehyde concentrations found in macerated oak mixtures.

are in these cases higher than 1 and range from 1.07 to 8.40.

In view of these results, the influence of adding caramel to brandies seems clear. Apart from increasing the concentration of 5-HMF, the content of which is high in caramel, the furfural/5-HMF ratio becomes higher than 1.

These results were verified by the AOAC technique for qualitative determination of caramel and by one-way ANOVA.

It was found that the method used for qualitative determination of caramel had a detection limit of 1 g $litre^{-1}$ of brandy. Lower concentrations were recorded as negative; in these cases the furfural/5-HMF ratio would still be less than 1, indicating caramel concentrations lower than the detection limit of the technique used.

The determination of caramel colour was positive in all the samples of commercial brandies analysed, except in samples 15 and 18 of the traditional series. These are the only commercial brandy samples in which the furfural/5-HMF ratio was higher than 1.

The influence of the presence of caramel on the furfural/5-HMF ratio therefore seems clear.

To confirm these results once again, they were submitted to statistical verification. This test is used in order to decide whether the differences found in the furfural/5-HMF ratios are a consequence of adding caramel or are simply accidental.

Before carrying out the statistical test, the distribution of the samples was checked by the Kolmogorov–Smirnov test (to estimate the degree of fit for normal representation). The samples presented a normal distribution and their significance level was 0.289 606. The ANOVA could then be run to check the influence of adding caramel on the furfural/5-HMF ratio. If a non-normal distribution of samples had been obtained, a non-parametric test such as Kruskal–Wallis analysis by ranks would have been applied.

Table 1. Results after applying the one-way ANOVA test

Source of variation	Sum of squares	d.f.	Mean square	*F*-ratio	Significance level
Between groups	116.22828	1	116.22828	58.392	0.0000
Within groups	99.52395	50	1.99048		
Total (corrected)	215.75223	51			

Missing value(s) have been excluded. d.f., degrees of freedom.

Table 2. Table of means for RATIO.brandies by RATIO.caramel

Level	Count	Average	Standard error (internal)	Standard error (pooled)	95% confidence intervals for mean	
Yes	36	0.1438611	0.0322262	0.2351406	−0.3285405	0.6162627
No	16	3.3831250	0.6397115	0.3527108	2.6745225	4.0917275
Total	52	1.1405577	0.1956488	0.1956488	0.7474958	1.5336196

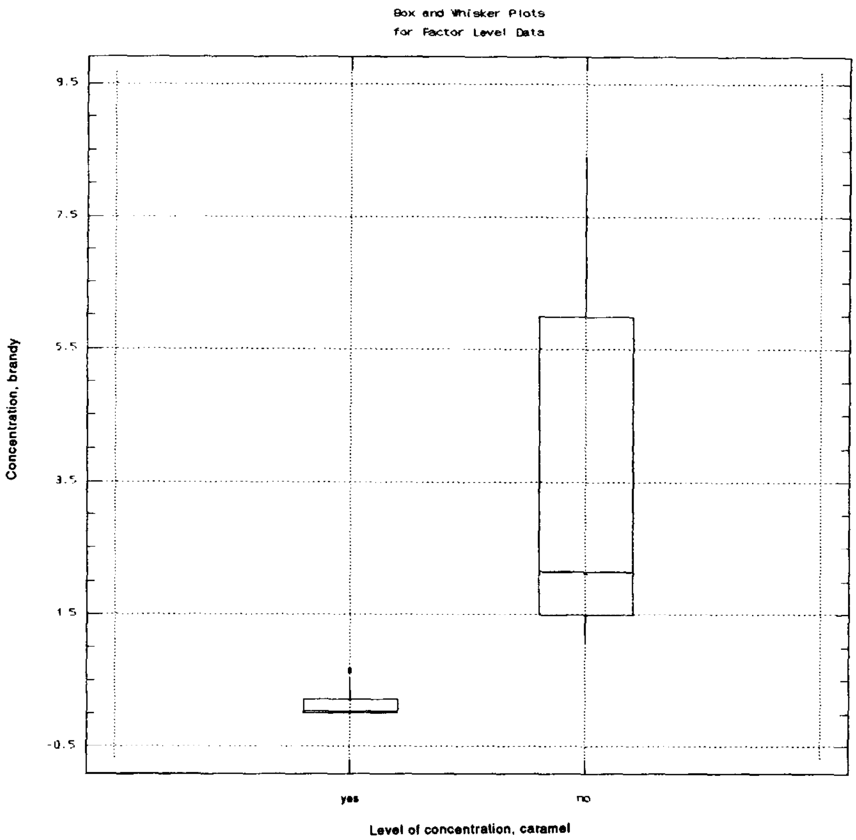


Fig. 3. Graphical representation of the results obtained from one-way ANOVA test.

The results of the ANOVA test are shown in Tables 1 and 2 and Fig. 3, and can be observed to be significant (significance level 0.0), revealing the influence of adding caramel colour on the furfural/5-HMF ratio.

CONCLUSIONS

If caramel colour is added to brandies, it definitely influences the sign of the furfural/5-HFM ratio, as it is higher than 1 in those brandies without caramel and lower than 1 in those with caramel. Moreover, this ratio indicates the origin of 5-HMF as either the result of thermolysis of cellulose (ratio higher than 1) or as a consequence of adding caramel as a colouring agent (ratio lower than 1).

We should also point out that most of the commercial samples analysed contain caramel as a colouring agent.

ACKNOWLEDGEMENTS

We should like to express our gratitude to Miss Paloma and Dr. R. I. MacCandless for their contribution to translating this manuscript.

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