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EVALUATION OF WINE BRANDIES AUTHENTICITY BY THE RELATIONSHIPS BETWEEN BENZOIC AND CINNAMIC ALDEHYDES AND BETWEEN FURANIC ALDEHYDES

AVALIAÇÃO DA GENUINIDADE DE AGUARDENTES VÍNICAS VELHAS ATRAVÉS DAS RELAÇÕES ENTRE ALDEÍDOS BENZÓICOS E CINÂMICOS E ENTRE ALDEÍDOS FURÂNICOS

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SUMMARY

Nowadays we are looking at the use of infinity of commercial products (namely vanillin, tannins and caramel) that are added to wines and brandies intending especially the shorting of their ageing in wooden barrels or even its imitation, mainly due to economic reasons. It is also searched the supposed improvement or alteration of wines and brandies sensorial properties in order to support the consumers preference. In this point of view, the assessment of aged wines and brandies authenticity becomes indispensable, being also evident the search of simple and secure indicators to evaluate the type of wood used in the ageing process. Many authors have used furanic derivatives contents and or wood phenolic compounds ratios as indicators of the authenticity of brandies and other alcoholic beverages. However, some studies stated that the extraction of these wood compounds depends on several factors. On the other hand, incorrect experimental designs and or the absence of factors interaction analysis frequently contribute to have not credible results. In the present work is analyzed the potential interest of the relationships between phenolic aldehydes and between furanic derivatives to assess the brandies authenticity, examining the influence of the botanical species (seven oaks and one chestnut), the toasting level (light, medium and strong) and the ageing time (during the first four years) in a Lourinhã brandy analyzed by HPLC. The benzoic/cinnamic aldehydes ratio appeared suitable to evaluate if the wood used in the ageing of brandy was chestnut or oak. Conversely, the furanic derivatives contents and their ratios cannot be used as wood ageing markers, since they are dependent on the interaction between the botanical species and the toasting level.

Key words: **brandy, woods, ageing, authenticity, phenolic aldehydes, furanic derivatives**

Palavras-Chave: aguardente, madeiras, envelhecimento, genuinidade, aldeídos fenólicos, aldeídos furânicos

INTRODUCTION

According to Joseph and Marché (1972) "the natural ageing of brandies is comparable to the fruit maturation, which needs a great period to develop its nectar. During this stage several chemical reactions of hydrolysis and oxidation can occur, conditioned by the intracellular respiration. Many of these reactions, due to their analogy, lead to compare the fruit pericarp to the wooden barrel. Furthermore, the phenomena are strictly associated and the process acceleration, by artificial means, usually origins a general unbalance and affects the quality". So, it means that the barrel is not a simple vessel; it rather has an essential role on the final product quality.

The majority of the authors considering that both the quality and the differentiation of brandies are mostly determined by the release and subsequent transformation of lignin derivatives (Guymon e Crowell, 1968; Bricout, 1971; Litchev, 1989; Jouret e Puech, 1975; Deibner *et al.*, 1976; Puech, 1987; Puech e Goffinet, 1987; Nishimura e Matsuyama, 1989; Viriot *et al.*, 1993; Kadim e Mannheim, 1999) and tannins (Moutounet *et al.*, 1989; Puech *et al.*, 1990a; Viriot *et al.*, 1993) from the wood to the brandy, due to their phisico-chemical and sensorial effects.

Nowadays we are looking at the use of infinity of commercial products (namely ageing agents, vanillin, tannins, almond shells, and caramel) that are added to wines and brandies intending especially the shorting of their ageing in wooden barrels or even its imitation, mainly due to economic reasons. It is also searched the supposed improvement or alteration of wines and brandies sensorial properties in order to support the consumers preference (closely related to fashion).

In this point of view, the assessment of the aged wines and brandies authenticity becomes indispensable, being also evident the search of simple and secure indicators to evaluate the type of wood used in the ageing process - oak or chestnut.

Many authors (Jeuring and Kuppers, 1980; Villalon-Mir *et al.*, 1992) have been used furanic derivatives contents as indicators of the authenticity of brandies and other alcoholic beverages. Wood phenolic compounds (derived from wood lignins and tannins) have also a great importance as wood ageing markers. The relationships between phenolic aldehydes contents and phenolic acids contents have been used for this purpose (Deibner *et al.*, 1976; Puech *et al.*, 1977; Gomez-Cordoves *et al.*, 1980; Puech e Jouret, 1982; Belchior *et al.*, 1984; Puech *et al.*, 1984; Delgado e Gomez-Cordoves, 1987; Delgado e Gomez-Cordoves, 1990; Calvo *et al.*, 1992; Vivas *et al.*, 1993; Vlassov e

Maruzhenkov, 1999). However, other studies (Guymon and Crowell, 1970; Guymon and Crowell, 1972; Onishi *et al.*, 1977; Quesada-Granados *et al.*, 1996) stated that the extraction of these wood compounds depends on several factors, such as the type of oak wood used for the barrel, the barrel size, the heat treatment of wooden barrels, and the ageing time. On the other hand, incorrect experimental designs and or the absence of factors interaction analysis frequently contribute to obtain not credible results. So, the main objective of this work is to analyze the potential interest of the relationships between benzoic aldehydes (vanillin and syringaldehyde) and cinnamic aldehydes (coniferaldehyde and sinapaldehyde), as well as the relationships between furanic derivatives (furfural and 5-hydroxymethylfurfural) to assess the brandies authenticity. In this perspective, it is examine the influence of the botanical species, the toasting level and the ageing time on these ratios in a *Lourinhã* brandy.

MATERIAL AND METHODS

Materials

Woods

The heartwood staves of seven different woods were seasoned in the open air, at a cooperage industry - JMA Gonçalves in the Northern of Portugal.

Their anatomical study (Carvalho, 1998) allowed to identify the botanical species: three Portuguese oaks, which were all *Quercus pyrenaica* Willd., from three different sites (**CNE**, **CNF** and **CNG**), two French oaks, one from "Limousin" was *Quercus robur* L. (**CFL**) and another from "Allier" was *Quercus sessiliflora* Salisb. (**CFA**), one American oak from the North America was a mixture of *Quercus alba* L./*Quercus stellata* Wangenh. and *Quercus lyrata* Walt. /*Quercus bicolor* Willd. (**CAM**) and one chestnut from the Northern of Portugal was *Castanea sativa* Mill. (**CAST**).

The staves were used to make nine barrels (250 L) of each wood. The barrels were then submitted to the heat treatment with three levels of toasting - light (**QL**), medium (**QM**) and strong (**QF**) - with three replications of each level. Prior to and after the heat treatment, each barrel sampling of wood was carried out gathering the wood chips, making a homogenous group with them and then keeping the sample.

Brandies

The barrels were placed in 1996 at *Adega Cooperativa de Lourinhã* in a similar cellar conditions and filled with the same *Lourinhã* brandy. The brandies sampling was made in the first (1997), second (1998), third (1999) and fourth (2000) year of ageing.

Methods

The wood extraction was performed as described by Canas *et al.* (1999).

Analysis of low molecular weight phenolic compounds and furanic derivatives by High Performance Liquid Chromatography

Samples of wood extracts and brandies were added with an internal standard (4-hydroxybenzaldehyde, 20 mg/l), filtered through 0,45 µm membrane (Titan) and analyzed by direct injection of 20 µl. Chromatography was performed as described by Canas *et al.* (2003), with a HPLC Lachrom Merck Hitachi system equipped with a quaternary pump L-7100, a column oven L-7350, a UV-Vis detector L-7400, and an autosampler L-7250, coupled to a HSM D-7000 software (Merck) for management, acquisition and treatment of data. A Merck Lichrospher RP18 (5 µm) column (250 mm x 4 mm i.d.) was used as the stationary phase.

Statistical analysis

The two-way analysis of variance was performed using Statistica vs '98 edition (Statsoft Inc., E.U.A.).

RESULTS AND DISCUSSION

Relationship between phenolic aldehydes

Woods

In all of the botanical species studied (non-toasted woods) the benzoic aldehydes relationship supplants very significantly the cinnamic aldehydes ones, with a less pronounced difference in *Limousin* oak (Fig. 1w).

The variance analysis also shows that the botanical species and the toasting level have a very significant influence on the benzoic/cinnamic aldehydes ratio in toasted woods. However, there is no significant interaction between these factors.

Comparing the mean proportions of benzoic/cinnamic aldehydes in non-toasted woods (Fig. 1w) and in the corresponding toasted woods (Fig. 1tw), one can verify that the toasting origins an important reduction of benzoic aldehydes and, complementarily, the increasing of cinnamic aldehydes. This fact could reflect the more important formation and or higher thermal stability of cinnamic compounds.

As the toasting intensity rises the proportion of cinnamic aldehydes increases and the proportion of benzoic aldehydes decreases (Fig. 2tw), as observed by Nishimura *et al.* (1983) in oak wood. It is possible to distinguish two clusters:

one formed by light toasted woods and another formed by medium and strong toasted woods.

Concerning the wood botanical species (Fig. 1tw), it is important to point out that toasting allows higher uniformity in chestnut wood, while unbalances the composition in oak woods towards cinnamic aldehydes. After the toasting, differences on benzoic/cinnamic aldehydes ratios between oaks become not significant and the difference between oaks and chestnut become significant.

Brandies

The results of variance analysis show that the botanical species, the toasting level and the ageing time have a very significant influence on the phenolic aldehydes percentages in brandies.

The increasing of benzoic aldehydes in oak aged brandies (Fig. 1b) relatively to the corresponding toasted woods (Fig. 1tw) could be due to some conditions that had permitted higher oxidation of cinnamic aldehydes proceeding from wood constituents' degradation by the toasting and released to the brandy. This phenomenon seemed to be decisive for brandies balance.

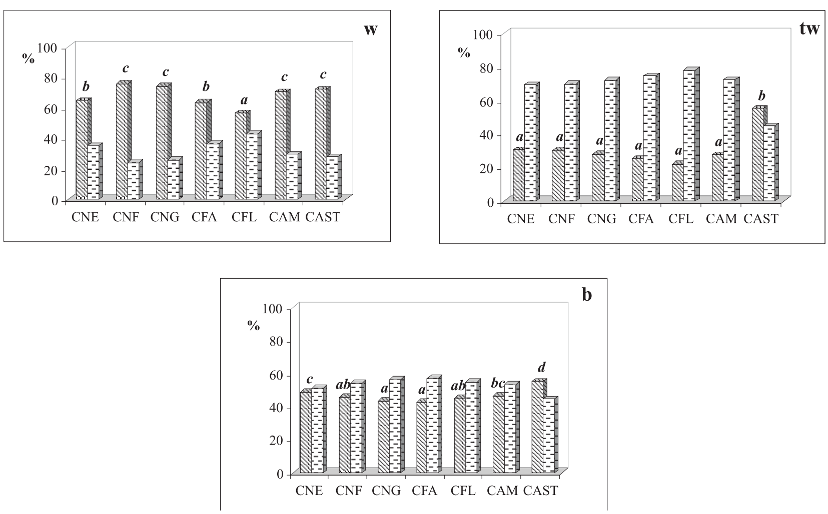

Fig. 1 - Proportion of benzoic and cinnamic aldehydes in different (w) untoasted woods, (tw) toasted woods and (b) aged brandies, as a function of the botanical species: benzoic aldehydes; cinnamic aldehydes. *Benzoic aldehydes bars with the same letter are not significantly different at α=0,01.*

Proporção de aldeídos benzóicos e cinâmicos em diferentes (w) madeiras não queimadas, (tw) madeiras queimadas e (b) aguardentes envelhecidas, em função da espécie botânica. A mesma letra nas barras correspondentes aos aldeídos benzóicos indica diferença não significativa com α=0,01.

This subject is somewhat controversial, as the results obtained by Deibner *et al.* (1976) in A*rmagnac*'s and R*um*'s and by Baldwin *et al.* (1967) in W*hiskies* indicated the predominance of cinnamic aldehydes, while those obtained by Puech *et al.* (1977) and Puech (1978) in A*rmagnac*'s and R*um*'s revealed the opposite. Attending to the relative antiquity of this studies and the technological advance occurred in the meantime, the differences could be partially justified by the analytical methodology.

The brandies aged in chestnut wood can be differentiated by the highest value of benzoic/cinnamic aldehydes ratio that is always higher than the unit. Particular attention must be paid because contradictory values can be observed in few cases. These deviations could be explained by the strong variability between brandies.

Fig. 2b shows the remarkable decreasing of benzoic aldehydes and, conversely, the increasing of cinnamic aldehydes, from light toasting to medium toasting aged brandies (mean values of one, two, three and four-years-aged brandies). The accumulation of cinnamic compounds is closely related to the synthesis supremacy comparatively to their degradation in the wood during the heat treatment (Canas, 2003) or throughout the brandy ageing process.

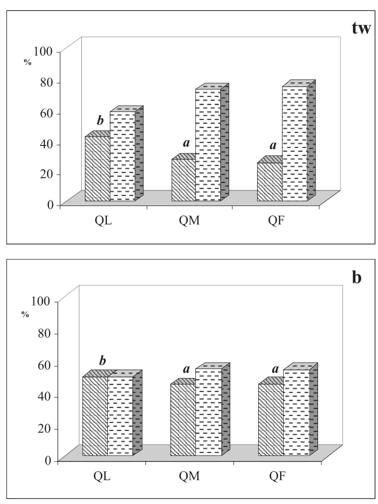

Fig. 2 - Proportion of benzoic and cinnamic aldehydes in (tw) toasted woods and (b) brandies, as a function of the toasting level: benzoic aldehydes; cinnamic aldehydes. *Benzoic aldehydes bars with the same letter are not significantly different at α=0,01.*

Proporção de aldeídos benzóicos e cinâmicos em (tw) madeiras queimadas e (b) aguardentes envelhecidas, em função do nível de queima. A mesma letra nas barras correspondentes aos aldeídos benzóicos indica diferença não significativa com α=0,01.

In contrast, Puech *et al.* (1992) observed that cinnamic aldehydes were lower in brandies aged in strong toasted wooden barrels than those aged in medium toasting wooden barrels. This discrepancy should be attributed to: the empiricism of heat treatment ; the wood inter and intraspecific variability; the brandies age; the analytical methodology used.

In one-year, two-years and three-years aged brandies is obvious the predominance of cinnamic aldehydes, although the continuous and significant increasing of benzoic aldehydes along with time (Fig. 3). The four-years aged brandies already present higher proportion of benzoic aldehydes than cinnamic aldehydes. This evolution reveals the importance of cinnamic aldehydes oxidation and or the progressive softening of their extraction, particularly of sinapaldehyde, from the wood (also showed by their kinetics).

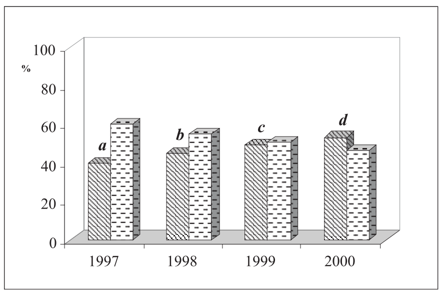

Fig. 3 - Proportion of benzoic and cinnamic aldehydes in (tw) toasted woods and (b) brandies, as a function of the toasting level: benzoic aldehydes; cinnamic aldehydes. *Benzoic aldehydes bars with the same letter are not significantly different at* α*=0,01.*

Proporção de aldeídos benzóicos e cinâmicos em (tw) madeiras queimadas e (b) aguardentes envelhecidas, em função do nível de queima. A mesma letra nas barras correspondentes aos aldeídos benzóicos indica diferença não significativa com α*=0,01.*

Some authors (Belchior *et al.*, 1984; Puech *et al.*, 1984; Calvo *et al.*, 1992) also reported the preponderance of cinnamic aldehydes in young brandies aged in new barrels and the increasing of benzoic ones along with ageing time. Similar effect was observed by Salagoity-Auguste (1992) in *Cognac's* during the first ten years of ageing in oak wood. Deibner *et al.* (1976) referred the high prevalence of cinnamic aldehydes in one-year aged A*rmagnac's* and *Rum*'s, and the tendency to their decreasing from the third to the fifteenth year of ageing. Nevertheless, studies performed by Puech *et al.* (1977) and Puech (1978) in the same beverages show that the proportion of benzoic aldehydes is always dominant, in spite of become less important along with the ageing time.

Analyzing the kinetics of extraction/oxidation of phenolic aldehydes in aged brandies (Fig. 4), it is interesting to verify the resemblance of the benzoic aldehydes kinetics, as well as the resemblance of the cinnamic aldehydes

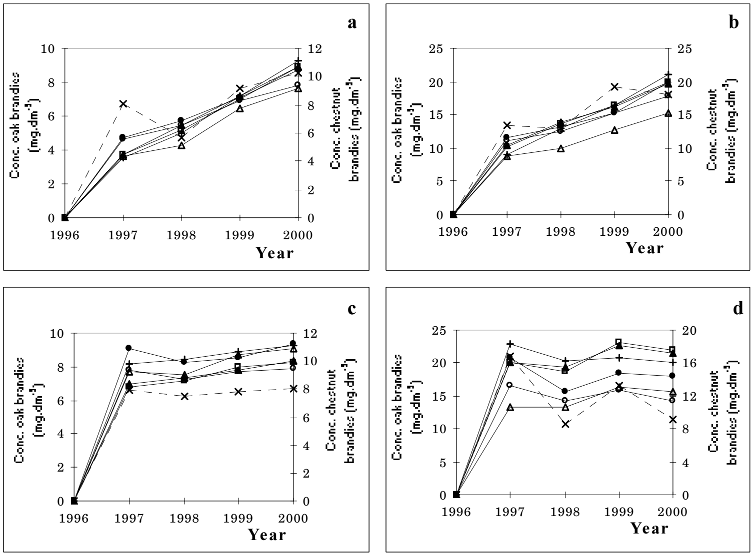

Fig. 4 - Kinetics of phenolic aldehydes in aged brandies, as a function of wood botanical species: (a) vanillin; (b) syringaldehyde; (c) coniferaldehyde; (d) sinapaldehyde; CNE; CNF; CNG; CFA; CFL; CAM; CAST.

Cinéticas de aldeídos fenólicos em aguardentes envelhecidas, em função da espécie botânica: (a) vanilina; (b) siringaldeído; (c) coniferaldeído; (d) sinapaldeído.

kinetics. In fact, the benzoic ones present a continuous increasing during the ageing period, while the cinnamic ones trend to stabilize from the second year on. This observation is coherent with those made by Salagoity-Auguste (1992) in *Cognac's* and by Calvo *et al.* (1992) in French brandies from one-year to eight-years ageing.

On the other hand, the kinetics of guayacil-type compounds (vanillin and coniferaldehyde) and the kinetics of syringyl-type compounds (syringaldehyde and sinapaldehyde) seemed to be linked, since the softening of coniferaldehyde and sinapaldehyde increments (Fig. 4c,d) correspond to a regular increasing of vanillin and syringaldehyde increments (Fig. 4a,b) respectively, from the second year on. Therefore, it can mean that after the first year of ageing the oxidative phenomena trends to exceed the extraction phenomena (Puech *et al.*, 1984), although extraction process already involves some oxidation (Belchior e San-Romão, 1982). This fact induces the balance dislocation towards benzoic aldehydes. Another hypothesis to explain that effect could be based on a more exhaustive extraction of coniferaldehyde and sinapaldehyde than vanillin and syringaldehyde from the wood. However, under the essayed conditions it was not possible to evaluate the depletion differences of wood on syringaldehyde and vanillin, as verified by Piggot *et al.* (1993).

Relationship between furanic derivatives

The results reveal that furfural is the most abundant furanic derivative, particularly in the brandies aged in *Q. pyrenaica* woods. The lowest content of furfural is detected in brandies aged in chestnut wood. Among the analyzed compounds is the only that already exists in the distilled (Onishi *et al.*, 1977; Jeuring e Kuppers, 1980), but is mainly derived from wood as a consequence of heat treatment (Canas, 2003). In fact, 5-hydroxymethylfurfural and 5-methylfurfural proceeding from the hexoses of cellulose and furfural derived from the pentoses, the main constituents of hemicelluloses (Hodge, 1967). As the hemicelluloses are the most thermosensitive polymers in wood (Fengel and Wegener, 1989) they are preferentially degraded during heat treatment, contributing to make furfural the main furanic derivative in toasted oak wood (Biermann *et al.*, 1987; Chatonnet, 1995) and in the corresponding aged brandies. In a previous work (Canas, 2003) we verified that 5-hydroxymethylfurfural was the most plentiful furanic compound in toasted wood, probably because it can derive from hexoses of other wood polysaccharides (Sarni *et al.*, 1991), although furfural was the most important compound in the corresponding aged brandies.

The highest 5-methylfurfural content corresponds to brandies aged in chestnut wood and allows their differentiation from those aged in oak woods.

Onishi *et al.* (1977) also concluded that furfural and 5-methylfurfural contents of brandies depend on the botanical species. These authors and Guymon and Crowell (1970, 1972) found higher contents in brandies aged in American oak than those aged in *Limousin* and *Allier* oaks, which contradict the results now obtained for furfural. This fact could also be explained by the strong intraespecific variability of the wood and by the methodological differences. The results obtained by Guymon and Crowell (1970, 1972), Quesada-Granados *et al.* (1996) and our results suggest that furfural and 5-methylfurfural contents cannot be used to distinguish the brandies aged in different woods, due to their dependence on several factors, such as the distilled, the wooden barrel type (new *versus* reused), the toasting and the kinetics of extraction/oxidation. Furthermore, the amounts of furfural, 5-hydroxymethylfurfural, and especially 5-methylfurfural, could increase with the addition of caramel to the brandy (Pons *et al.*, 1991; Vilallon Mir *et al.*, 1992; Quesada-Granados *et al.*, 1996), so that they should not be used as wood ageing markers. Consequently, these authors considered that the furfural/5-methylfurfural relationship could be used to evaluated brandies authenticity - understanding authentic product as the one obtained by a natural ageing process. Nonetheless, the results now obtained (Table I) indicate that is not correct to generalize that a furfural/5-methylfurfural ratio lower than the unit is a consequence of caramel supplement (Vilallon Mir

TABLE I

Minimum, maximum and mean values of the furfural/5-methylfurfural ratio in aged brandies

Valores máximos, mínimos e médios da relação furfural/5-metilfurfural em aguardentes envelhecidas

	furfural/5-methylfurfural ratio		
	min	max	mean
Botanical species (**)			
CNE	6,97	28,86	13,29 ***bc***
CNF	7,25	22,28	11,40 ***b***
CNG	8,06	22,47	12,43 ***bc***
CFA	8,73	48,26	14,83 ***c***
CFL	7,03	25,70	10,82 ***b***
CAM	6,34	22,66	10,41 ***b***
CAST	0,29	20,95	5,65 ***a***
Toasting level(**)			
QL	0,29	48,26	14,71 ***b***
QM	2,32	20,95	10,12 ***a***
QF	1,17	13,25	8,95 ***a***
Ageing time (ns)			
1997	3,00	25,25	12,14
1998	4,29	28,86	11,89
1999	0,57	20,95	9,22
2000	0,29	48,26	11,80

*Values for means calculation: wood - 24; toasting – 56; time – 42; Means followed by the same letter in a column are not significantly different at α=0,01**; ns = without significant difference.*

et al., 1992). In fact, under one natural ageing process, this ratio is lower than the unit in brandies aged in chestnut wood, due to its richness on 5-methylfurfural. Some brandies aged in light toasting wooden barrels also presented that characteristic. Moreover, the relationship between these two furanic derivatives depends significantly on the botanical species and the toasting level.

Confront with other analytical parameters, such as the dry extract, and the syringaldehyde and vanillin contents (Belchior *et al.*, 1984) seems to be indispensable to the accurate analysis of brandies authenticity.

CONCLUSIONS

In the essayed conditions (brandies with the same age and aged in new barrels), the benzoic/cinnamic aldehydes ratio appeared suitable to evaluate if the wood used in the ageing of brandy was chestnut or oak, showing a tendency to be higher than the unit in the first case and lower than the unit in the second. No significant interaction between the botanical species, the toasting level and the ageing time on this ratio supports this conclusion.

The furanic derivatives contents and their ratios cannot be used as wood ageing markers, since they are dependent on the interaction between the botanical species and the toasting level. The appreciation of brandies authenticity based on furfural/5-methylfurfural ratio is not credible because it could be lower than the unit without caramel addition, as observed in brandies aged in chestnut and in light toasting wooden barrels.

Nevertheless, it was only examined three factors and one brandy. Thus, further experiments are required to test the relationships between phenolic aldehydes and between furanic derivatives in brandies: from different provenances; with different age; aged in reused barrels; aged in other woods.

ACKNOWLEDGEMENTS

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RESUMO

Avaliação da genuinidade de aguardentes vínicas através das relações entre aldeídos benzóicos e cinâmicos e entre aldeídos furânicos

Assiste-se actualmente ao uso de uma infinidade de produtos comerciais (nomeadamente vanilina, taninos e caramelo) que são adicionados a vinhos e a aguardentes com a intenção de encurtar o tempo de envelhecimento em madeira ou mesmo à sua imitação, principalmente por razões de ordem económica. Com o seu uso procura-se também a suposta melhoria ou alteração das características organolépticas de vinhos e aguardentes, no sentido de satisfazer o gosto do consumidor. Neste sentido, torna-se indispensável a apreciação da genuinidade de vinhos e aguardentes, sendo também premente a procura de indicadores simples e fiáveis para a avaliação do tipo de madeira usado no envelhecimento. Muitos autores têm recorrido aos teores de aldeídos furânicos e/ou às relações entre os compostos fenólicos da madeira como indicadores da genuinidade de aguardentes e de outras bebidas alcoólicas. Contudo, alguns estudos indicam que a extracção dos compostos da madeira depende de diversos factores e, por outro lado, delineamentos experimentais incorrectos e/ou a ausência da análise da interacção dos factores comprometem a credibilidade dos resultados obtidos. Neste trabalho é analisado o interesse potencial das razões entre aldeídos fenólicos e entre aldeídos furânicos para a avaliação da genuinidade das aguardentes, através da apreciação da influência das espécies botânicas (sete madeiras de carvalhos e uma de castanheiro), do nível de queima (ligeira, média e forte) e do tempo de envelhecimento (durante quatro anos) numa aguardente *Lourinhã* analisada por HPLC. A razão aldeídos benzóicos/cinâmicos parece adequada para avaliar se no envelhecimento foi usada madeira de castanheiro ou de carvalho. Contrariamente, os teores e as razões de aldeídos furânicos não podem ser usados como marcadores do envelhecimento em madeira face à sua estreita associação a factores interdependentes como a espécie botânica e o nível de queima.

RÉSUMÉ

Evaluation de l'authenticité des eaux-de-vie de vin par les relations entre aldéhydes benzoïques et cinnamiques et entre aldéhydes furaniques

De nos jours, on constate l'utilisation d'un grand nombre de produits commerciaux (vanilline, tanins et caramel) qui sont additionnés aux vins et aux eaux-de-vie dans le but de réduire la durée de vieillissement sous bois ou de simuler ce vieillissement pour des raisons économiques. On cherche également à améliorer ou à modifier les caractéristiques organoleptiques des vins et des eaux-de-vie afin de satisfaire le goût du consommateur. Dans cette perspective, évaluer l'authenticité du vieillissement des vins et des eaux-de-vie devient indispensable. De plus, il est nécessaire de posséder des indices simples et fiables afin d'évaluer le type de bois utilisé lors du vieillissement. De nombreux auteurs ont utilisé les teneurs en aldéhydes furaniques et/ou les relations entre composés phénoliques du bois comme facteurs d'authenticité pour les eaux-de-vie et autres boissons alcooliques. Cependant, certaines études ont démontré que l'extraction de ces composés dépend de différents facteurs. D'autre part, des protocoles expérimentaux inadaptés et/ou l'absence de l'analyse de l'interaction des facteurs n'ont pas toujours fourni de réponses crédibles. Dans ce travail on analyse l'intérêt des relations entre aldehydes phénoliques et entre aldehydes furaniques pour évaluer l'authenticité des eaux-de-vie, en étudiant l'influence des espèces botaniques (sept chênes et un chatagnier), du niveau de brûlage (léger, moyen et fort) et du temps de vieillissement (pendant quatre années) dans une eaux-de-vie *Lourinhã* analysée par HPLC. Le rapport aldéhydes benzoïques/cinnamiques apparaît correct pour estimer si le bois utilisé lors du vieillissement des eaux de vie est le châtaignier ou le chêne. A l'inverse, les aldehydes furaniques ne peuvent pas être utilisés comme marqueurs du vieillissement sous bois car ils dépendent de différents facteurs interdépendants tel que l'espèce botanique et le niveau de brûlage.

REFERENCES

Baldwin S., Black R. A., Andreasen A. A., Adams S. L., 1967. Aromatic congener formation in maturation of alcoholic distillates. *J. Agr. Food Chem.*, **15**, 381-385.

Belchior A. P., San-Romão V., 1982. Influence de l'oxygène et de la lumière sur l'évolution de la composition phénolique des eaux-de-vie vieillis en bois de chêne. *Bull. Liasion Groupe Poyphenols*, **11**, 598-604.

Belchior A. P., Puech J-L., Carvalho E., Mondies, H., 1984. Caractéristiques de la composition phénolique du bois de chêne portugais et de quelques eaux-de-vie de vin. *Cienc. Tec. Vitiv.*, **2**, 57-65.

Biermann C. S., Mc Ginnis G., Schultz T. P., 1987. Scanning electron microscopy of mixed hardwoods subjected to various pretreatment processes. *J. Agr. Food Chem.*, **35**, 713-716.

Bricout J., 1971. Analyse de quelques constituants dérivés du chêne dans les vieillis eaux-de-vie d'Armagnac. *Ann. Technol. Agric.*, **20**, 217-224.

Calvo A., Caumeil M., Pineau J., 1992. Extraction des polyphénols et des aldéhydes aromatiques pendant le vieillissement du cognac, en fonction du titre alcoolique et du "degré d'épuisement" des fûts. *In: Elaboration et connaissance des spiritueux*. 562 - 566. Cantagrel R. (ed.), Lavoisier - Tec & Doc, Paris.

Canas S., 2003. *Estudo dos compostos extraíveis de madeiras (Carvalho e Castanheiro) e dos processos de extracção na perspectiva do envelhecimento em Enologia.* 303 p. Tese de Doutoramento em Engenharia Agro-Industrial, Instituto Superior de Agronomia, Universidade Técnica de Lisboa.

Canas S., Leandro M.C., Spranger M.I., Belchior A.P., 1999. Low molecular weight organic compounds of chestnut wood (*Castanea sativa* L.) and corresponding aged brandies. *J. Agric. Food Chem.*, **47**, 5023-5030.

Canas S., Belchior A.P., Spranger M.I., Bruno de Sousa R., 2003. High-performance liquid chromatography method for analysis of phenolic acids, phenolic aldehydes and furanic derivatives in brandies. Development and validation. *J. Sep. Sci.*, **26**, 496-502.

Carvalho A., 1998. Identificação anatómica e caracterização física e mecânica das madeiras utilizadas no fabrico de quartolas para produção de aguardentes velhas de qualidade - denominação Lourinhã. *Ciência Tec. Vitiv.,* **13**, 71-105.

Chatonnet, P., 1995. *Influence des procédés de tonnellerie et des conditions d'élevage sur la composition et la qualité des vins élevés en fûts de chêne*. 268 p. Thèse doctorat de l'Université de Bordeaux II, Institut d'œnologie.

Deibner L., Jouret C., Puech J.-L., 1976. Substances phénoliques des eaux-de-vie d'Armagnac. I. La lignin d'extraction et les produits de sa dégradation. *Ind. Alim. Agric.*, 401-414.

Delgado T., Gomez-Cordoves C., 1987. Teneur des brandies commerciaux espagnols en aldéhydes et en acids phénoliques. *R. F. Oenol.*, **107** (cahier scientific), 39-43.

Delgado T., Gomez-Cordoves C., Villarroya B., 1990. Relationships between phenolic compounds of low molecular weight as indicators of the aging conditions and quality of brandies. *Am. J. Enol. Vit.*, **41**, 342-345.

Fengel D., Wegner G., 1989. *Wood. Chemistry, Ultrastructure, Reactions*. 612 p. Walter de Gruyter, Berlin.

Gomez-Cordoves C., Hernandez Mt., Calera J.G., 1980. Application de la CLPH a l'étude des eaux-de-vie. *Bull. Liasion Groupe Poyphenols*, **10**, 252-258.

Guymon J. F., Crowell E. A., 1968. Separations of vanillin, syringaldehyde and other aromatic compounds in the extracts of French and American oak woods by brandy and aqueous alcohol solutions. *Qual. Plant. Materiae*, **16**, 302-333.

Guymon J.F., Crowell E.A., 1970. Brandy aging. Some comparisons of American and French oak cooperage. *Wines & vines*, 23-25.

Guymon J. F., Crowell E. A., 1972. GC-separated brandy components derived from French and American oaks. *Am. J. Enol. Vit.*, **23**, 114-120.

Hodge J. E., 1967. Origin of flavour in foods. Nonenzymic browning reactions. *In: Chemistry and Physics of flavour,* 465-491, Schultz H. W., Day E. A., Libey L. M. (Eds.), AVI Publis. Co, Westport.

Jeuring H. J., Kuppers J. E. M., 1980. High performance liquid chromatography of furfural and hydroxymethylfurfural in spirits and honey. *J. Assoc. Off. Anal. Chem.*, **63**, 1215-1218.

Joseph E., Marché M., 1972. Contribution à l'étude du vieillissement du Cognac. Identification de la scopolétine, de l'aesculétine, de l'ombelliférone, de la β-méthyl-ombelliférone, de l'aesculine et de la scopoline, hétérosides provenant du bois. *Conn. Vigne Vin*, **6**, 1-58.

Jouret C., Puech J.-L., 1975. Importance de la lignine dans le vieillissement des rhums. *Ann. Technol. Agric.*, **24**, 325-333.

Kadim D., Mannheim C. H., 1999. Kinetics of phenolic extraction during aging of model wine solution and white wine in oak barrels. *Am. J. Enol. Vit.*, **50**, 33-39.

Litchev V., 1989. Influence of oxidation processes on the development of the taste and flavor of wine distillates. *Am. J. Enol. Vit.*, **40**, 31-35.

Moutounet M., Rabier P., Puech J.-L., Varette E., Barillère J.-M., 1989. Analysis by HPLC of extractable substances in oak wood. Application to a chardonnay wine. *Sci. Alim*, **9**, 35-51.

Nishimura K., Matsuyama R., 1989. Maturation and maturation chemistry. *In: The science and technology of whiskies*, cap 8, 235-263, Piggott J. R., Sharp R., Duncan R. E. B. (Eds.), Longman Scientific & Technical, Essex.

Nishimura K., Ohnishi M., Masahiro M., Kunimasa K., Ryuichi M. (1983). Reactions of wood components during maturation. *In: Flavour of distilled beverages: origin and development,* 241-255, Piggott, J. R. (Ed.), Ellis Horwood Limited, Chichester.

Onishi M., Guymon J. F., Crowell E. A., 1977. Changes in some volatile constituents of brandy during aging. *Am. J. Enol. Vit.*, **28**, 152-158.

Piggot J. R., Conner J. M , Peterson A., Clayne J., 1993. Effects on scotch whisky composition and flavour of maturation in oak casks with varying histories. *Int. J. Food Sci. Tecn.*, **28**, 303-318.

Pons I., Garrault C., Jaubert J.-N. Morel J., Fenyo J.-C., 1991. Analysis of aromatic caramel. *Food Chem.*, **39**, 311-320.

Puech J-L., 1978. *Vieillissement des eaux-de-vie en fûts de chêne. Extraction et évolution de la lignine et de ses produits de dégradation*. 68 p. Thèse doctorat de l'Université Paul Sabatier de Toulouse.

Puech J.-L., 1987. Extraction of phenolic compounds from oak wood in model solutions and evolution of aromatic aldehydes in wines aged in oak barrels. *Am. J. Enol. Vit.*, **38**, 236-238.

Puech J.-L., Goffinet B., 1987. Adjustment of nonlinear models for lignin and its degradation products during the aging of Armagnac. *J. Food Sci.*, **52,** 1280-1282, 1301.

Puech J.-L., Jouret C., Deibner L., Alibert G., 1977. Substances phénoliques des eaux-de-vie d'Armagnac et de rhum. II. Produits de la degradation de la lignin: les aldéhydes et les acides aromatiques. *Ind. Alim. Agric.*, 483-493.

Puech J.-L., Jouret C., 1982. Dosage des aldéhydes aromatiques des eaux-de-vie conservées en fûts de chêne: détection d'adultération. *Ann. Fals. Exp. Chim.*, **805**, 81-90.

Puech, J.-L., Lepoutre, J.-P., Baumes, R., Bayonove, C, & Moutounet, M., 1992. Influence du thermotraitement des barriques sur l'évolution de quelques composants issus du bois de chêne dans les eaux-de-vie. *In: Élaboration et connaissance des spiritueux*, 583-594, R. Cantagrel (Ed.), Lavoisier-Tec & Doc.,Paris.

Puech J.-L, Leauté R., Clot G., Nomdedeu L., Mondies H., 1984. Évolution de divers constituants volatiles et phénoliques des eaux de vie de cognac au cours de leur vieillissement. *Sci. Aliments*, **4**, 65-80.

Puech J.-L , Rabier P., Bories-Azeau J., Sarni F., Moutounet M., 1990. Determination of ellagitannins in extracts of oak wood and in distilled beverages matured in oak barrels. *J. Assoc. Off. Anal. Chem.*, **73**, 498-501.

Quesada Granados J., Villalón Mir M., García-Serrana L., Pólez Martínez M. C., 1996. Influence of aging factors on the furanic aldehyde contents of matured brandies: aging markers. *J. Agr. Food Chem.*, **44**, 1378-1381.

Salagoity-Auguste M. H., 1992. La scopolétine: un marqueur de la conservation en fûts de chêne. *Vigne et vin publ. Intern.*, 105-113.

Sarni F., Moutounet M., Puech J.-L., 1991. Composés phénoliques extractibles de copeaux de bois de chêne. *In: Les eaux-de-vie traditionnelles d'origine viticole*, 231-239, Bertrand, A. (Ed.), Lavoisier - TEC & DOC, Paris.

Villalón Mir, Quesada Granados J., López Gª De La Serrana H., López Martinez M. C., 1992. High performance liquid chromatography determination of furanic compounds in commercial brandies and caramels. *J. Liq. Chromat.*, **15**, 513-524.

Viriot C., Scalbert A., Lapierre C., Moutounet M., 1993. Ellagitannins and lignins in aging of spirits in oak barrels. *J. Agr. Food Chem.*, **41**, 1872-1879.

Vivas N., Chauvet S., Sudraud P., Glories Y., 1993. Techniques de contrôle et d'évaluation de la qualité des tanins œnologiques. *Ann. Fals. Exp. Chim.,* **919**, 215-222.

Vlassov V. N., Maruzhenkov D. S., 1999. Application of GC/MS method for the identification of brandies and cognacs. *Analusis*, **27**, 663-667.