

Influence of Distillation System, Oak Wood Type, and Aging Time on Volatile Compounds of Cider Brandy

ROBERTO RODRÍGUEZ MADRERA,[†] DOMINGO BLANCO GOMIS,[‡] AND
 JUAN J. MANGAS ALONSO^{*,†}

Servicio Regional de Investigación y Desarrollo Agroalimentario (SERIDA),
 E-33300 Villaviciosa, Spain and Departamento de Química Física y Analítica, Facultad de Química,
 Universidad de Oviedo, E-33006 Oviedo, Spain

A study of the influence of distillation system, oak wood type, and aging time on volatile compounds of cider brandy was carried out. Acetaldehyde and acetaldehyde diethyl acetal were influenced by distillation technology, oak wood type, and maturation time. The majority ester, ethyl ethanoate, increased during aging, the highest level of this ester being detected in spirits distilled by double distillation. The alcohols of higher molecular weight were better recovered in the rectification column than in the double distillation system. Ethanoate esters decreased throughout aging of the spirits, and their degradation velocity was lower in distillates obtained from double distillation. Fatty acids and their ethyl esters presented the opposite evolution during aging, detecting an increase in ethyl esters and a decrease in their corresponding fatty acids. An increase of 1,1,3-triethoxypropane was detected during aging. French oak contributes the trans isomer of β -methyl- γ -octalactone and American oak contributes the cis isomer.

KEYWORDS: Volatile components; distillation; oak; aging; cider brandy

INTRODUCTION

Cider brandy is a common drink in Western European regions where apple cultivars are viable. Like other distilled beverages (fruit brandies, cognac, whisky, etc.), it is characterized by the presence of volatile compounds (esters, alcohol, acids, and carbonyl compounds) that mainly originate during the fermentation and distillation stages, and to a smaller extent during aging.

During the prefermentative and fermentative stages, several compounds are incorporated into the fermented products: On one hand, flavors present in the fruit and those developed during extraction of the juice (such as terpene derivatives and varietal compounds); on the other, fermentation aromas formed by the action of yeast (fusel oils, fatty acids, esters, etc). Thus, for example, an extended maceration time and the use of glycosidases led to an increase in flavor compounds in raw material, improving varietal characterization in grape distillates (1). An intense enzymatic treatment employed in manufacturing apple juice concentrate for cider production originates higher levels of methanol than when fresh must is employed (2). In relation to the fermentation process, the temperature must be lower than 20 °C to avoid the loss of aromatic substances (3, 4). Moreover, the choice of an appropriate yeast strain could give rise to brandies with a desired aromatic profile, due to the effect that the yeast lees have on the ratio of aroma compounds between

the base wine and the distillates (5). Likewise, depending on the medium conditions, yeast strains can generate H₂S, and because of the high reactivity of this nucleophilic compound, yield sulfides during distillation (6), favored by the presence of copper (7). These substances, known for their nauseous character, disappear via oxidation and evaporation during the maturation of whisky (8), improving the sensorial perception of distillates.

The distillation process not only concentrates the volatile constituents from fermentation but also produces new compounds via esterification, dehydration, etc. Thus, furfural increases when a pot still is employed, and reactions can take place on the plates of a continuous still that can modify the neutral ester composition of the distillate (9). Other congeners such as pyrazines, derived from the Maillard reaction, and furanic compounds, derived from the degradation of residual sugars, are related to aromas such as cacao and caramel, respectively; their levels in brandies are higher in pot stills, in which the heat period is longer (10). It should likewise be pointed out that acrolein, responsible for the "peppery" character in rum, whisky, and brandy, is a thermal degradation product of glycerol and is also produced by bacterial action on fermented beverages (11–13).

The components of fresh spirit react during the maturation period, favored by the high ethanol content. Thus, the concentration of ethyl ester of fatty acids increases with aging, but esters of other alcohols, like 3-methyl-1-butyl ethanoate, decrease by transesterification (9, 14). These volatile esters have

* To whom correspondence should be addressed. Tel.:34-985890066.
 Fax: 34-985891854. E-mail: juanjoma@princast.es.

[†] SERIDA.

[‡] Universidad de Oviedo.

pleasant fruity odors and low thresholds, improving the organoleptic characteristics of distillates.

An important volatile compound present in beverages matured in oak wood is oak lactone (β -methyl- γ -octalactone). Masson et al. (15) identified a precursor of this compound in sessile oak, a European white oak species used for cooperage. Only (3*S*, 4*S*) and (3*S*, 4*R*) stereoisomers are found in brandies (16), and the ratio between has been employed to characterize brandies matured in French or American oak (17–19). Its odor is defined as coconut and woody by Chatonnet (20), and the thresholds values are 0.067 and 0.79 mg/L for *cis* and *trans* isomers, respectively (21).

Today, volatile compounds in distillates are determined by GC and direct injection where concentrations are higher than 10 mg/L; for lower levels, concentration of the sample prior to GC analysis by rapid techniques such as microextraction (14) or solid-phase microextraction (SPME) (22, 23) is necessary.

In this paper, we study the influence of the distillation system, oak type, and aging time on the concentration of volatile compounds in cider brandy.

MATERIALS AND METHODS

Reagents. All standards were of analytical quality. Ethyl esters were supplied by Fluka (Busch, Switzerland), acetaldehyde by Merck (Darmstadt, Germany), fatty acids by Sigma (Madrid, Spain), and alcohols, ethanoate esters, 1,1,3-triethoxypropane, racemic β -methyl- γ -octalactone mixture, acetaldehyde diethyl acetal, and 3-methyl-1-butyl octanoate by Aldrich (Madrid, Spain).

Standards. Major Volatile. Standard solutions were prepared in ethanol/water (65:35). Samples and standards were filtered through a 0.45- μ m PVDF (poly(vinylidene difluoride)) membrane. 3-Pentanol was used as internal standard at 0.5 g/L. Samples were directly injected into the GC system.

Minor Volatile. Standard solutions were prepared in ethanol/water (30:70), and filtered through a 0.45- μ m PVDF membrane. Samples were subjected to microextraction with Freon 113, according to the method optimized by Ferreira et al. (24). Ten milliliters of cider brandy, previously diluted to 30% (v/v) in ethanol, were introduced into the extraction centrifuge tubes jointly with 150- μ L of Freon 113, 2 g of ammonium sulfate and 5- μ L of a solution of 2-ethyl-1-hexanol (13 g/L in ethanol at 30%, v/v, internal standard). The tubes were shaken by means of a 1024 water shaking bath at 20 °C for 60 min and centrifuged (12 000g, for 10 min). One microliter of the organic phase was recovered and injected into the chromatographic system.

GC Equipment and Conditions. Major Volatile. The following equipment and column were used for GC analysis of the major volatile: a Hewlett-Packard 5890 gas chromatograph fitted with a flame ionization detector and 5 m \times 1/8 in. stainless steel column packed with carbowax 1500 on carbowax C 8/100 to 0.5%. Chromatographic conditions were as follows: initial temperature, 45 °C for 10 min; program rate, 3.5 °C/min; final temperature, 125 °C; isothermal to 125 °C for 25 min; injector and detector temperature, 170 °C; carrier gas, He at 60 psi; injection volume, 1 μ L.

Minor Volatile. The following equipment and column were used for GC analysis of the minor volatile: a Hewlett-Packard 5890 gas chromatograph interfaced with a mass selective detector (MSD) Hewlett-Packard 5972, fitted with a column (FFAP 50 m \times 0.22 mm i.d.; phase thickness, 0.33 μ m), and inserted into a split/splitless injector (splitless time, 1 min). Chromatographic conditions were as follows: initial temperature, 40 °C for 5 min; program rate, 3.0 °C/min; final temperature, 220 °C; isothermal to 220 °C for 60 min; injector and detector temperature, 250 °C; carrier gas, He at 1 mL/min; injection volume, 1 μ L. The analyses were performed in the electron impact (EI) mode, and the ionization voltage was fixed at 70 eV. The recovery levels for the analytes studied ranged between 83 and 114% and the relative standard deviations were smaller than 7.5% (14).

Raw Material. 20 000 L of cider was made from apple juice concentrate (AJC). The AJC was diluted with water (density of

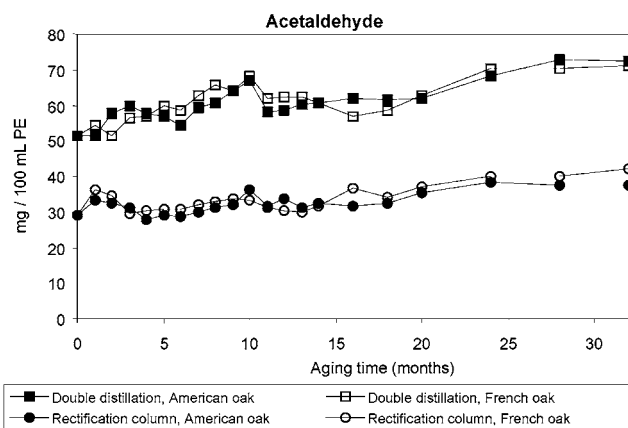


Figure 1. Changes in acetaldehyde content during aging. PE = pure ethanol.

reconstituted apple juice, 1056 g/L), and fermented by a starter of *Saccharomyces cerevisiae* belonging to the SERIDA microorganisms collection. The cider was distilled employing two methods (double distillation and a rectification column system) and the distillates were matured in wood casks (twelve experimental units) of French (*Quercus sessilis*) and American oak (*Quercus alba*) for 32 months. American oak came from Ohio and French oak from the Allier forest. The wood, once brushed and cut, was subjected to a light toasting (20 min at 180 °C). The thickness of the staves and cask capacities were 28 mm and 120 L, respectively.

Experimental Design. A factorial design (2 \times 2) with three replicates was used. The factors or independent variables studied were as follows: distillation system (two levels, double and rectification column), wood (two levels, French oak and American oak), and aging time (21 samplings for 32 months). Response variables were as follows: (1) major volatile (acetaldehyde, acetaldehyde diethyl acetal, ethyl ethanoate, methanol, 1-propanol, 1-butanol, 2-methyl-1-propanol, 2-methyl-1-butanol, and 3-methyl-1-butanol) and (2) minor volatile (ethyl 3-methylbutanoate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate, ethyl hexadecanoate, ethyl 9,12-octadecadienoate, diethyl butanedioate, 3-methyl-1-butyl ethanoate, hexyl ethanoate, 2-phenylethyl ethanoate, 3-methyl-1-butyl octanoate, 1-hexanol, 1-octanol, 1,1,3-triethoxypropane, *cis* and *trans* β -methyl- γ -octalactone, octanoic acid, decanoic acid, dodecanoic acid, tetradecanoic acid, and hexadecanoic acid). Statistical treatment (25) consisted of an ANOVA with two factors and two levels. An ANOVA for the time factor was carried out for each combination (distillation \times wood). Duncan's multiple range test was carried out for pairwise comparisons among means. Differences were considered significant at the 5%.

RESULTS AND DISCUSSION

Major Volatile. Acetaldehyde and acetaldehyde diethyl acetal are two chemically related molecules that were influenced by the factors studied (distillation system, wood, and aging time). The use of a double distillation technique (Charente type) produced higher levels of acetaldehyde and acetaldehyde diethyl acetal than when the rectification still system was used, which could be related to the higher distillation time of double distillation (Figures 1 and 2). At the same time, with the use of double distillation, an increase in acetaldehyde was observed during aging (Figure 1) that may be a consequence of ethanol oxidation and acetaldehyde diethyl acetal hydrolysis (Figure 2). The increase in acetaldehyde during aging was less important when the rectification column system was employed; the synthesis of acetaldehyde diethyl acetal could probably have some effect on this fact. The influence of oak wood type on acetaldehyde was detected in the first phases of the aging process (9 months of aging), detecting a greater concentration of this

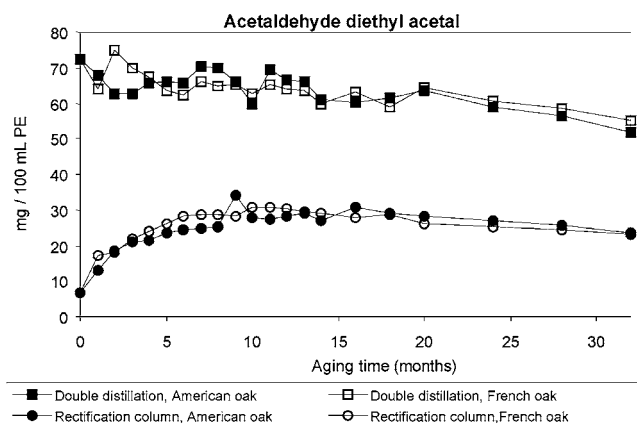


Figure 2. Changes in acetaldehyde diethyl acetal content during aging. PE = pure ethanol.

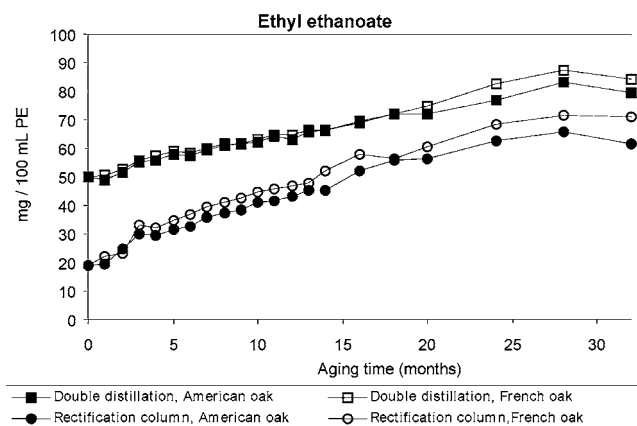


Figure 3. Changes in ethyl ethanoate content during aging. PE = pure ethanol.

molecule with French oak, which could be related to the larger pore size of the staves, permitting the passage of a higher concentration of oxygen. As is well known, the woods of *Quercus sessilis* and *Quercus pedunculata* species (French oak) are more porous than that of *Quercus alba* species (American oak). The evolution of acetaldehyde diethyl acetal during aging was influenced by its initial concentration. Thus, hydrolysis occurs if the initial concentration is high, whereas synthesis develops when the initial concentration is low (Figure 2).

Transesterification of ethanoate esters and esterification of ethanoic acid by ethanol are two processes that may explain the significant increase detected in ethyl ethanoate during the aging process (Figure 3). At the same time, the distillation system had a significant influence on the ethyl ethanoate content, detecting a higher level when a double distillation system was employed (Figure 3). From two years of aging on, a significant influence was detected of oak wood type on ethyl ethanoate concentration. French oak provided the highest concentration of this ester, irrespective of the distillation technology used, which could be related to the larger pore size of the staves, which facilitated oxidation of ethanol to ethanoic acid. The ethyl ethanoate concentration detected in the experimental cider brandies was smaller than that reported by Guichard et al. (26) in freshly distilled Calvados. These authors established that a high esters to ethyl ethanoate ratio can be of prime importance for good quality.

Alcohols (methanol and higher alcohols) were influenced by the distillation system employed in different ways. By means of the Charente-type distillation, methanol and 1-butanol were recovered in higher proportions, the contrary being observed

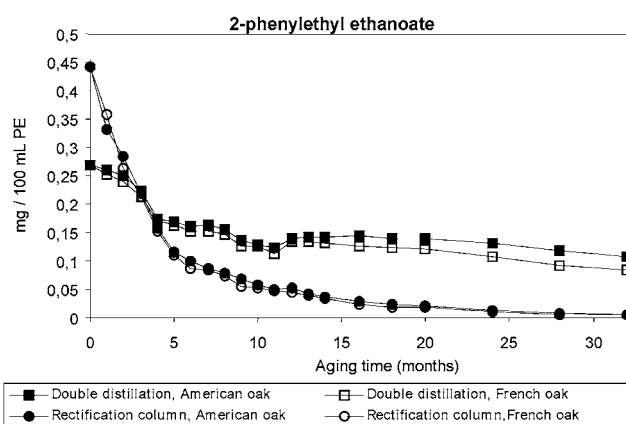


Figure 4. Changes in 2-phenylethyl ethanoate content during aging. PE = pure ethanol.

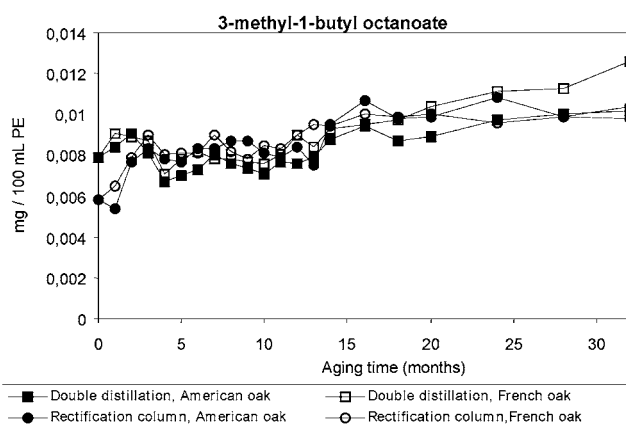


Figure 5. Changes in 3-methyl-1-butyl octanoate content during aging. PE = pure ethanol.

for 1-propanol, 2-methyl-1-propanol and 2 and 3-methyl-1-butanol. In this sense, it may be pointed out that a decrease in the higher alcohol content was also observed in marc spirits using a redistillation technique (27).

Minor Volatile. Ethanoate esters such as 3-methyl-1-butyl, hexyl, and 2-phenylethyl were influenced by aging time and distillation system, although in the case of the 2-phenylethyl ethanoate, a significant interaction between distillation and wood factor was also observed. Normally, a decrease in ethanoate esters was detected during the aging process (Figure 4), which is in accordance with the results obtained in brandy by Onishi et al. (9). Distillates obtained from double distillation presented a degradation velocity of ethanoate esters lower than those produced with the rectification column still. This fact could be explained if we take into account the fact that distillates obtained by means of the column had a more acid pH (pH 2.8) than those obtained by double distillation (pH 3.5). As is well known, the transesterification process is a reaction catalyzed in acid media. At the same time, the transesterification phenomenon was not observed in 3-methyl-1-butyl octanoate. In fact, the concentration of this ester increased during the aging process (Figure 5). Probably, steric hindrance of the acid and alcohol chains on nucleophilic attack of ethanol could hinder said process.

The use of the double distillation system produced a higher concentration of fatty acids (octanoic, decanoic, dodecanoic, tetradecanoic, and hexadecanoic), which subsequently decreased during the aging process (Figure 6). The opposite occurred as regards the evolution of the ethyl esters of fatty acids (3-methylbutanoate, hexanoate, octanoate, decanoate, dodecanoate,

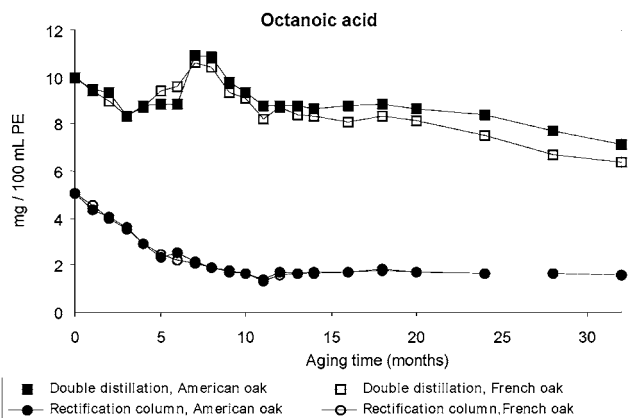


Figure 6. Changes in octanoic acid content during aging. PE = pure ethanol.

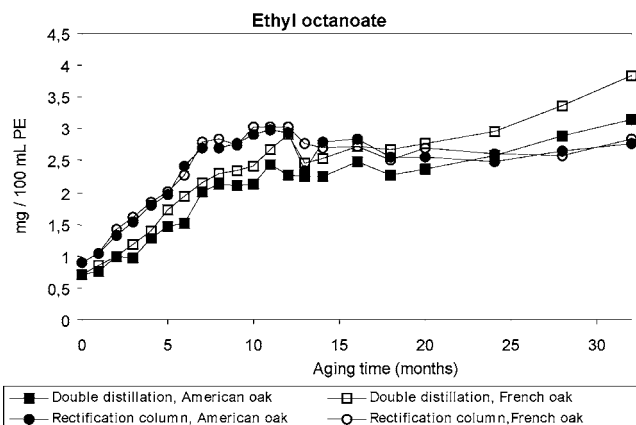


Figure 7. Changes in ethyl octanoate content during aging. PE = pure ethanol.

tetradecanoate, and hexadecanoate) with aging time, because an increase was detected in all cases (Figure 7). However, this evolution was conditioned by the distillation technology employed. As can be seen in Figure 7, distillates obtained via the rectification column system presented a maximum concentration of ethyl esters around 12 months of aging. This maximum is coincidental with the stabilization of the fatty acids level observed in this phase of aging (Figure 6). Equilibrium of the esterification reaction is obtained more rapidly in distillates manufactured via the rectification column technique, probably as a consequence of their lower pH. As is well-known, the esterification reaction is catalyzed by the hydrogen ion. The decrease in fatty acids, defined as soapy and fat, and the increase in their ethyl esters, defined as fruity, during the aging process involve important changes from the point of view of sensorial properties of cider brandy.

Other minor volatiles, such as ethyl 9,12-octadecadienoate, diethyl butanedioate, 1,1,3-triethoxypropane, β -methyl- γ -octalactones (cis and trans), 1-octanol, and 1-hexanol, were also studied. In relation to ethyl 9–12-octadecadienoate, it may be pointed out that all three factors studied (distillation, oak wood, and aging time) influenced its concentration. An increase in this analyte with aging was observed, detecting significant differences for distillation and oak wood factors from 14 months of aging (Figure 8). In this sense, we quantified the highest concentration of this ester in distillates aged in French oak wood and distilled by the rectification column system (Figure 8). The concentration of diethyl butanedioate was dependent on distillation technology and aging time. As we can see in Figure 9, the double distillation system extracted a greater concentration

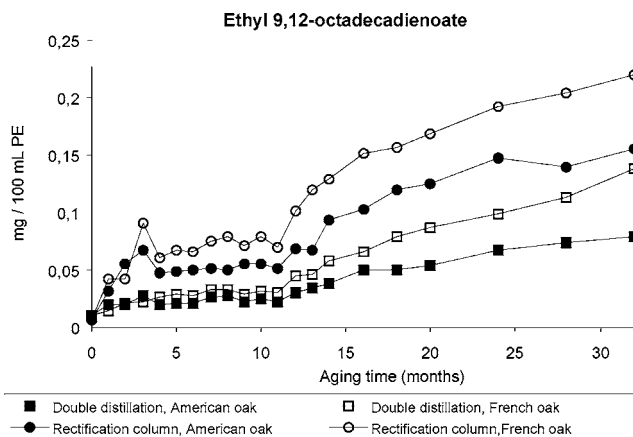


Figure 8. Changes in ethyl 9,12-octadecadienoate content during aging. PE = pure ethanol.

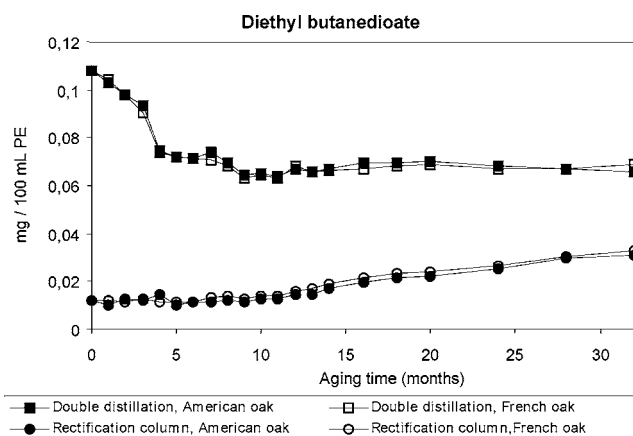


Figure 9. Changes in diethyl butanedioate content during aging. PE = pure ethanol.

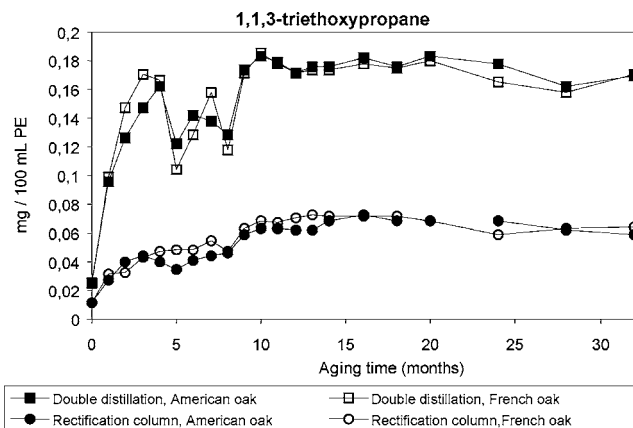


Figure 10. Changes in 1,1,3-triethoxypropane content during aging. PE = pure ethanol.

of this ester, and the use of the rectification still system accumulated diethyl butanedioate at the end of the aging process. In distillates manufactured from the double distillation system, hydrolysis of this ester was detected throughout the first 10 months of aging (Figure 9). 1,1,3-Triethoxypropane is the molecule that results from the acetalization process of acrolein by ethanol in an acid medium. This acetal was influenced by aging time and distillation system (Figure 10). 1,1,3-Triethoxypropane was accumulated during the first 10 months of the aging process, its concentration being higher in distillates elaborated via the double distillation system. It is likely that the lower rectification capacity of this technology in relation to

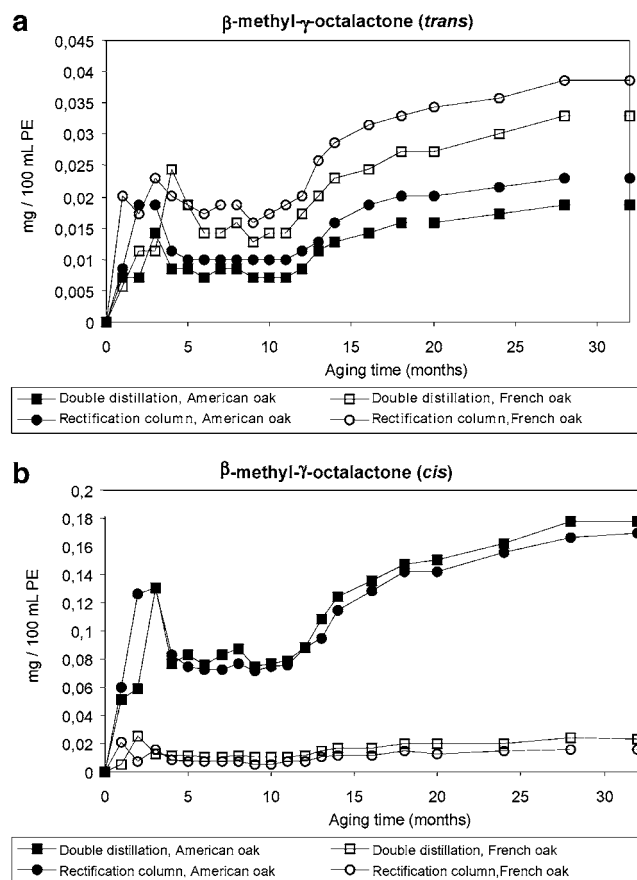


Figure 11. (a) Changes in β -methyl- γ -octalactone (trans) content during aging. PE = pure ethanol. (b) Changes in β -methyl- γ -octalactone (cis) content during aging.

the rectification column system would cause a higher accumulation of acrolein in the fresh distillate (fact not confirmed), which might justify the higher level of acetal detected in the distillates elaborated using the double distillation system (Figure 10). A high concentration of 1,1,3-triethoxypropane can decrease the sensory quality of cider brandy, as described in Calvados, where an "acrolein" defect was associated to this acetal (28). The hypothetical decrease in acrolein during aging as a consequence of synthesis of 1,1,3-triethoxypropane would influence the improvement of the sensory quality of cider brandy, since acrolein is a pungent and lachrymatory compound, while acetals are pleasant and fruity.

Oak lactones (cis and trans isomers of β -methyl- γ -octalactone) have a characteristic oak-wood aroma perceptible at very low concentrations. Thermal degradation of the inner face of the staves produces a layer of active carbon that increases the yield of β -methyl- γ -octalactones. In our study, both lactones were influenced by aging time and oak wood type. Figure 11a and 11b shows the concentration of cis and trans β -methyl- γ -octalactone in the distillates studied during the aging process. Trans β -methyl- γ -octalactone is principally contributed by French oak wood, while American oak wood basically contributes the cis β -methyl- γ -octalactone. These results show the possible utility of these molecules for differentiating cider brandies aged in French and American oak wood. In this sense, Guichard et al. (16) pointed out the influence of the origin of the wood (American white oak from Kentucky and French oak from Limousin forest) on the amount of β -methyl- γ -octalactone. Brandies matured in American white oak contained a greater amount of the cis isomer than those matured in French oak. Furthermore, Masson et al. (17) showed the effects of oak

species on the contents of cis and total β -methyl- γ -octalactone and on the proportion of the cis isomer in wood extracts, being higher in American oak. Likewise, we have detected an increase of β -methyl- γ -octalactones during the aging process. If we take into account the threshold concentration of β -methyl- γ -octalactones and the quantities of these accumulated in the experimental cider brandies, we may conclude that only in the case of cider brandies aged in American oak wood could the aromatic contribution of these molecules be perceived.

The minor alcohols, 1-hexanol and 1-octanol, presented differentiated behavior depending on the distillation system. While the double distillation system extracted a greater quantity of 1-hexanol, the contrary was observed for 1-octanol. During the first steps of maturation process, a decrease in the concentration of these alcohols was detected.

In conclusion, the double distillation system produces higher concentrations of acetaldehyde, acetaldehyde diethyl acetal, 1,1,3-triethoxypropane, diethyl butanedioate, and ethyl ethanoate than the rectification column still, probably as a consequence of the lower rectification capacity and the longer distillation time employed in the double distillation technology. Distillates obtained from double distillation also present higher concentrations of fatty acids. Normally, higher alcohol is recovered in greater proportions in the rectification column still. The degradation velocity of ethanoate esters from a transesterification process is higher in the distillates obtained from the rectification column still, probably as a consequence of lower pH values detected in these spirits. French oak facilitated the oxidation process, probably due to the larger pore size of the staves in relation to American oak casks; distillates aged in French oak casks accumulate higher quantities of ethyl ethanoate. Trans β -methyl- γ -octalactone is principally extracted from French oak, while the contrary is observed for cis β -methyl- γ -octalactone in American oak. Hence, these analytes could be used to distinguish cider brandies on the basis of the wood type employed in their maturation.

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