BIO Web of Conferences **56**, 02013 (2023) https://doi.org/10.1051/bioconf/20235602013
43rd World Congress of Vine and Wine

Ellagitannin evolution of aged Cognac eaux-de-vie; Impact of barrel toasting

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Abstract. The contribution of *C*-glucosidic ellagitannin-derived compounds to eaux-de-vie quality has been recently demonstrated. However, there is a gap in our knowledge of the content, composition, and evolution of these compounds in this specific matrix. The objective of this study was therefore to carry out an analysis of the kinetics of these compounds, and to study how they are impacted by barrel toasting. For this purpose, barrels representing eight different to asting levels were used to age the same eau-de-vie during the first 18 months. Ellagitannin quantification was carried out by HPLC-QQQ. The results showed that *C*-glucosidic ellagitannins were extracted during the first 3 months of aging and then decreased, whereas ellagitannin-derived spirit compound concentrations increased throughout aging. In addition, barrel toasting had such an impact on ellagitannin content that barrels were differentiated according to their levels.

1 Introduction

Ellagitannins have a specific structure composed of an open-chain glucose esterified in position 4 and 6 by a hexahydroxydiphenoyl unit (HHDP), and a nonahydroxyterphenoyl (NHTP) unit esterified in position 2, 3, and 5. The NHTP isalsolinked by a *C*-glycoside bond at the carbon-1 atom to the open-chain glucose core [1] (Fig. 1).

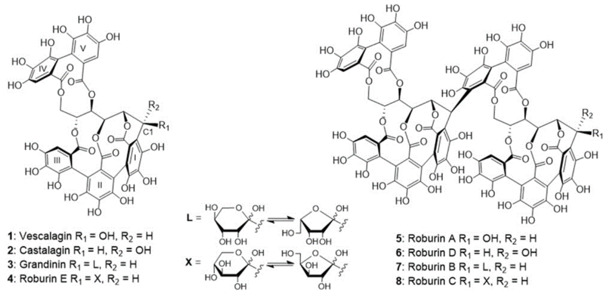

Figure 1. Structure of the eight C-glucosidic ellagitannins.

C-glucosidic ellagitannins are found in various concentrations in wood. These variations are the result of different factors, such as botanical species, geographical origin, single-tree variability, sampling position in the tree, grain, and processing of the wood in the cooperage [2–4]. All these parameters will have an impact on *C*-glucosidic ellagitannin concentrations, which may also influence the sensory profile of barrel-aged wines or spirits [2–5]. Among these, the toasting results in a thermodegradation of wood constituents. In general, the more the toasting increases, the greater the changes in ellagitannin content and composition [6–7]. Recently, eight individual ellagitannins were identified and quantified for the first time in Cognac eaux-de-vie [8].

Moreover, ellagitannin behavior during Cognac eaux-de-vie aging was studied and new *C*-glucosidic ellagitannin-derived compounds were found [9].

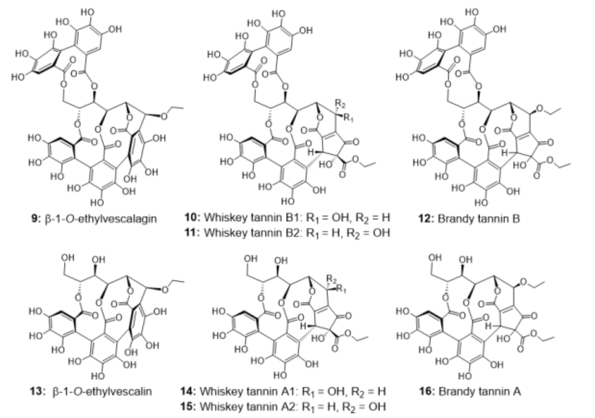

Figure 2. Structure of ellagitannin-derived spirit compounds (9-12) and their hydrolysis form (13-16) identified and quantified in Cognac eau-de-vie aged in contact with oak wood.

Given the limited knowledge of the concentrations, composition, and evolution of *C*-glucosidic ellagitannins in Cognac eaux-de-vie and the recent characterization of new oxidative ellagitannin compounds, the objective of this study was to monitor and compare the extraction kinetics of the eight known native oak C-glucosidic ellagitannins (1-8) and of the new ellagitannin-derived spirit compounds (9-16) in various eaux-de-vie aged in oak barrels with different toasting levels. The evolution kinetics of the above oak *C*-glucosidic ellagitannins were monitored for the first 18 months of aging. The influence of toasting level on *C*-glucosidic ellagitannin composition during aging of the same eau-de-vie in barrels was also studied.

2 Materials and methods

2.1 Cognac eaux-de-vie samples

Thirty-two 400 L oak wood barrels were manufactured with different toasting levels. Eight different toasting levels were studied, and four barrel replicates were produced and used for each level. The eight toasting levels studied consisted of four toasting temperatures (light, medium, medium plus and high) and two toasting durations (normal and slow) for each temperature (Table 1). Sampling was realized at 1 month (T1), 3 months (T2), 6 months (T3), 9 months (T4), 12 months (T5), and 18 months (T6) of aging.

Table 1. Description of the types of barrel toasting levels (Gadrat et al. [10]).

Toast	Notation	Sum °C.min
Light toast normal	LTN	3560
Light toast slow	LTS	5036
Medium toast normal	MTN	4566
Medium toast slow	MTS	5134
Medium toast plus normal	MT+N	5088
Medium toast plus slow	MT+S	6015
High toast normal	HTN	6892
High toast slow	HTS	7320

2.2 HPLC-UV-QQQ analysis

For the quantification of C-glucosidic ellagitannins in Cognac eaux-de-vie, the method had been developed and validated beforehand, as described previously [10].

2.3 Statistical treatment

All the statistical treatments were performed using Rstudio software (Rstudio Inc., Boston, USA, 2018). Normality and homocedasticity of the residuals were evaluated for all parameters, using the Shapiro–Wilk test and Levene's test, respectively [10].

3 Results and Discussion

3.1 Evolution of C-glucosidic ellagitannins and ellagitannin derived compounds in Cognac eaux-de-vie during aging

The evolution of *C*-glucosidic ellagitannins was studied during eau-de-vie aging for 18 months (Fig. 3). As it can be seen in Figure 3, independant of the toasting, the maximum concentration of *C*-glucosidic ellagitannins was reached at 3 months in barrel-aged red wines.

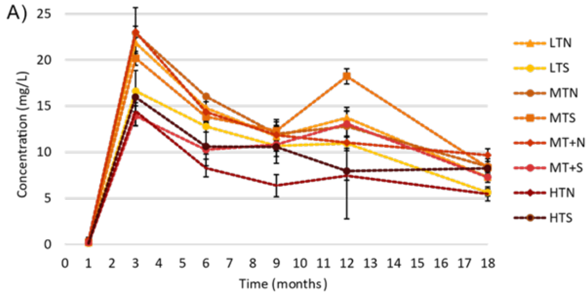

Figure 3. Sum of the C-glucosidic ellagitannin (1-8) concentrations in eau-de-vie during 18 months of aging in oak barrels manufactured with different toasting levels (A) (Gadrat et al. [10]).

Regarding the formation of the ellagitannin-derived spirit compounds from vescalagin and castalagin, the sum of the concentrations of the eight ellagitannin-derived spirit compounds during 18 months of aging is represented in Figure 4.

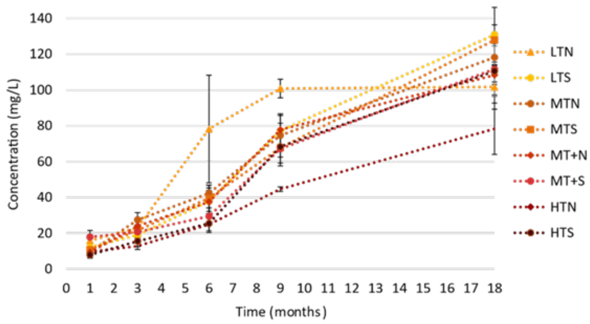

Figure 4. Sum of ellagitannin-derived spirit compound (9-14) concentrations in eau-de-vie during 18 months of aging in oak barrels manufactured with different toasting levels (Gadrat et al. [10]).

Regardless of toasting level, the concentrations of these compounds followed the same trend, i.e. their concentrations increased continuously during the 18 months of aging. In order to see the behaviour of each ellagitannin-derived spirit compound the concentration of each ellagitannin-derived spirit is plotted for the different sampling times. An exemple for the eau-de-vie aged in the MT+Nisshown in Figure 5. During the first 3 months of aging, the main ellagitannin-derived spirit compounds observed in the eau-de-vie were the non-HHDP-hydrolyzedones, i.e. whiskey tannins B1 and B2, brandy tannin B and β-1-O-ethylvescalagin, as their concentrations increased strongly (by between 69% and 87%) in the first 3 months, while those without HHDP moieties, such as whiskey tannins A1 and A2, brandy tannin A and β-1-O-ethylvescalin increased by between 37% and 49%.

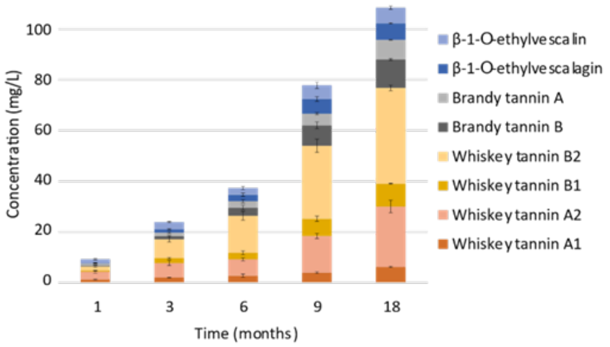

Figure 5. Behavior of ellagitannin-derived spirit compounds in the eau-de-vie for MT+N toasted barrel (Gadrat et al. [10]).

On the contrary, during the second phase of these kinetics, between 9 and 18 months, the concentrations of whiskey tannins A1 and A2 and these of brandy tannin A increased more rapidly (by between 36% and 40%) than those of whiskey tannins B1 and B2, and those of brandy tannin B (by between 23% and 28%).

3.2 Impact of the barrel toasting level on C-glucosidic ellagitannins and ellagitannin-derived spirit compounds

The impact of barrel toasting level on *C*-glucosidic ellagitannin content and composition was investigated. *C*-glucosidic ellagitannin concentrations were represented for each toasting level at 3 months of aging since their concentrations were the highest (Fig. 6). All eight *C*-glucosidic ellagitannins were impacted by the toasting level. In general, high toasting levels (HTN and HTS) resulted in lower ellagitannin contents.

Similarly, the impact of toasting level on concentrations of the ellagitannin-derived spirit compounds was studied, at 18 months of aging, when their concentrations were the highest (Fig. 7).

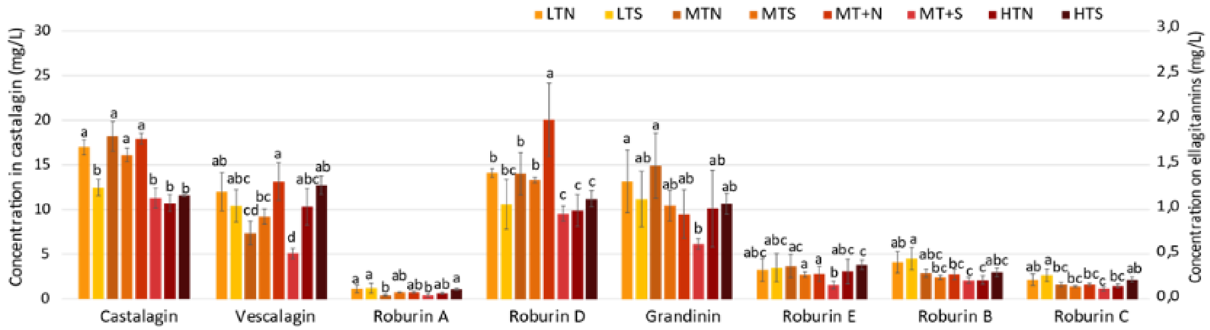

Figure 6. Impact of barrel toasting on concentrations of the C-glucosidicellagitannins in eau-de-vie at 3 months of aging (Gadrat et al. [10]).

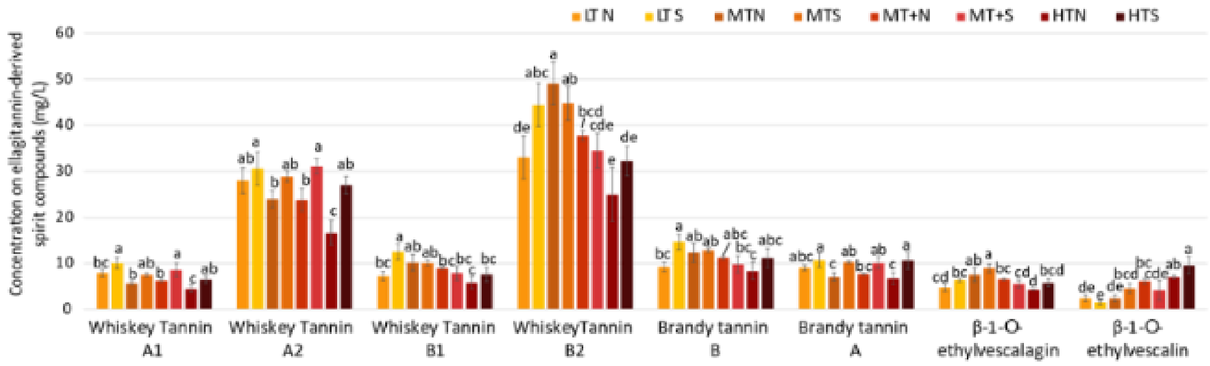

Figure 7. Impact of barrel toasting on concentrations of the ellagitannin derived spirit compounds in eau-de-vie at 18 months of ageing (Gadrat et al. [10]).

Longer aging seems accentuate the differences in *C*-glucosidic ellagitannin concentrations according to toasting level, because although the *C*-glucosidic ellagitannins were transformed over time, levels of ellagitannin-derived spirit compounds during aging were strongly dependent on toasting level. The differences observed among the toasting levels were more pronounced after 18 months, and toasting length has as well a strong impact on these compounds. A high toasting temperature favored β-1-*O*-ethylvescalin formation as this was the only ellagitannin derivative whose content increased significantly with toasting.

4 Conclusion

Kinetics of sixteen *C*-glucosidic ellagitannins were analyzed for the first time in Cognac eaux-de-vie after 18 months of aging. The influence of barrels toasting level on ellagitannin content was also studied. The eight oak *C*-glucosidic ellagitannins increased during the first three months and then decreased gradually. Regarding the ellagitannin-derived spirit compounds, their levels increased with aging time. During the first three months of aging, their non-hydrolyzed forms, such as whiskey tannin B, brandy tannin B, and *β*-1-O-ethylvescalagin, were predominant. After 9 months, however, their hydrolyzed forms, such as whiskey tannins A1, A2,and brandy tannin A formed faster. Concerning toasting influence, toasting length had a strong impact on these compounds, mainly after 18 months. Slow toasting gave rise to more ellagitannin extraction than normal toasting. Overall, a clear toasting differentiation was observed by ellagitannin levels, with HTN samples indicating the highest *β*-1-O-ethylvescalin levels, in particular.

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