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SHORT NOTE

REGULATION OF EXTRACTIVES CONTENT WITHIN OAK WOOD USED FOR BARRIQUE PRODUCTION BY SPECIFIC VARIATION OF RAW MATERIAL-AND PROCESS PARAMETERS

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ABSTRACT

In order to guarantee a maximum quality standard of oak-barrel stored wine, (barrique), the optimization of defined phenolic and non-phenolic wood compounds (e. g. whiskey lactones), which are released into the wine during storage, is necessary to enable its unique barrique taste. Numerous factors play a crucial role for the formation of these substances within wood. Besides the origin of the wood material, also storage/drying time and defined further processing parameters are responsible for its extract composition. In the present work, oak from three different sources, which had been stored/dried for different periods, was subjected to a successively increased thermal treatment (steaming, toasting). It could be shown, that especially whiskey lactones, those wood substances, which have a decisive influence on the wine-flavor, can be controlled or increased by deliberate selection of the raw material as well as processing parameters in the course of barrel production.

KEYWORDS: Phenolic compounds, oak wood, toasting, extractives analytics, barrique wine-production, whiskey lactones.

INTRODUCTION

The importance of oak wood for the production of wine barrels has been curtailed in the recent year as the use of storage tanks made from easier-to-use stainless steel and plastics had increased. However, the trend is nowadays pointing again towards the use of wood, primarily oak wood, for the production of so-called barriques (small barrels made from oak wood) for the storage of high-quality wines (Schusser and Schwanninger 2006a). Especially, wood from the sessile oak (*Quercus petraea* (Matt.) Liebl), is playing an important role in the production of wine barrels, as it combines important features such as compactness, close-grain and a high content of aromatic substances for guaranteeing the necessary product quality. Barrique barrels are produced in elaborate processes taking into account strict quality criteria (careful selection of the wood origin, wood drying/wood storage time). Furthermore, the woods' chemical composition changes throughout the heat treatment processes in the course of the barrel manufacturing, a process, which is also referred to as "toasting". During this process, wood flavors and as result flavors of the stored wine are intensified in order to achieve the desired specific wine taste (Dumitriu et al. 2017, Navarro et al. 2018). Especially the wood tannins are responsible for creating the round, smoothly taste of barrique wines (Scheiblhofer 2006). However, in recent years, other substances have gained increasing interest. Various flavors have been shown to count for the assessment criteria of the wine quality: the coconut-like whiskey lactones (stereoisomers -cis and trans), clove-like odors/flavors such as eugenol, spice-like aromas (guaiacol), caramel-like flavors (furfural), and vanillin, syringaldehyde (wild berries) and coniferyl aldehyde (cinnamon). To optimize the composition of these flavoring compounds is of utmost importance for ensuring a maximum wine-quality standard.

Many parameters influence the intensity of these flavors: Besides the factors oak species, wood origin (location factors) and the respective storage conditions/drying periods (Schusser et al. 2006), also product characteristics that emerge in the course of the processing of the raw material are responsible for the extract composition and thus the wine taste (Hale et al. 1999, Martinez et al. 1996). This study aims at the identification of parameters influencing the composition of phenolic and non-phenolic substances in oak wood. Besides the wood origin, special focus was also laid on the variation of drying time of the raw-material and the subsequent thermal processing-steps in the course of barrel production (toasting, steaming). The results of the research are supposed to enable the definition of future, clearly defined processing parameters for oak wood barrels in order to consistently ensure the maximization of the flavoring substances (e. g. the increasingly interesting whiskey lactones) of the wine stored therein.

MATERIALS AND METHODS

The raw material used was provided by Fassbinderei VBS Schön in Sitzenberg-Reidling, Lower Austria. Oak wood (*Quercus petrae*) from three different origins (Austria, Bosnia and Croatia) and after different drying times (1-3 years) was compared to fresh, never dried material from the same origin. All material was dried at the company site in Lower Austria. For the investigation of the processing steps, three different grades of toasting (*light, medium and heavy)* were applied and compared to steamed wood.

During the production of barrels from the corresponding raw materials, the following procedure was applied: barrels were made from staves out of the respective raw materials and initially steamed inside with water vapor for a period of three hours. After completion of the

steaming step two staves were removed from different sites of the barrel to determine their extractives composition. Subsequently, the remaining barrel was subjected to a routine toasting process in three successive stages, each of them increasing the degree of toasting (*light, medium, heavy*). After each stage, another two staves were removed for extractives determination and the remaining barrel was subjected to the next toasting step.

The removed stave sections (11 x 9 x 7 cm) were then extracted with suitable solvents: For this purpose, slices of 3-5 mm were cut off by means of a band saw on the wine facing side of the stave and crushed into chips with a thickness of about 1-2 mm, which were subsequently ground using an ultra-centrifugal mill (Retsch ZM 200) with a sieve size of 0.25 mm. All samples were deep-frozen after milling and lyophilized for 24 hours (Lyophille: Christ, Alpha 1-4 LD plus). 30 g of each sample was subjected to the extraction procedure: For each sample, two parallel extractions were performed. For this purpose, 120 mL of ethanol (denatured) was mixed with 5 $g \cdot L^{-1}$ (+) - tartaric acid and 800 mL of distilled water, and the pH of the solution was adjusted to 3.5 with NaOH. Afterwards, 0.25 ml of the internal standard (150 µl 1-octanol in 10 ml ethanol) was added and filled up to a volume of 1 L with distilled water. The samples were extracted for a period of one week in 250 mL of the extraction solution, filtered, transferred to a separatory funnel and extracted several times with dichloromethane (all reagents: Sigma Aldrich). The resulting extract was concentrated to approximately 1 mL in a Rotavapor® (Büchi, R-300 Multivapor P-6) and measured with GC-FID (Agilent 7890 A). The quantification of the ingredients was based on the corresponding standards (Sigma Aldrich), related to the internal standard 1-octanol, for the following substances: furfural, guaiacol, whiskey lactone-trans, whiskey lactone-cis, eugenol, vanillin, syringaldehyde, coniferyl aldehyde) and was performed according to the methods of Marco et al. (1994), after slight adaptation (temperature gradient adapted to separation column HP5MS: 100°C for 1 min, 5°C·min^{-1} to 200°C, 13°C·min^{-1} to 325°C).

RESULTS AND DISCUSSION

Fig. 1 shows the extractives of the "reference" oak samples from the three origins after different drying times. The fresh, as well as the 1- and 2-years dried samples from the origin Bosnia showed a very similar composition with respect to the ingredients furfural, coniferyl aldehyde, syringaldehyde, vanillin and the two whiskey lactones (-cis and -trans). The 3-years dried sample displayed a lower amount of furfural and, compared to the shorter dried samples, a substantially lower proportion of both whiskey lactones. Only very small amounts of eugenol and guaiacol were found in the investigated samples. The ratio between the whiskey lactones changed with the drying time.

In case of the origin Austrian the 1-year dried sample showed a significantly higher total amount of furfural, coniferyl aldehyde, syringaldehyde and vanillin and an extremely high amount of both whiskey lactones. However, these were found in only small amounts in the samples from Austria after 2 and 3 years of drying. The relative composition of substances was similar for all dried wood samples, except for the whiskey lactones, and was mainly comprising furfural, coniferyl aldehyde, syringaldehyde and vanillin. Fresh wood samples from Austria showed a relatively low content of syringaldehyde and coniferyl aldehyde as well as vanillin.

In case of the origin Croatia, the 3-years dried oak sample showed a significantly higher total amount of extractives than the other samples. Above all, the furfural content was very high after the long drying time. Strikingly, no furfural was found in the 1-year dried oak sample. In the fresh oak sample from the origin Croatia more whiskey lactone-cis was found than in the

other samples. For this origin, the qualitative composition was very similar in the samples fresh and 2- and 3-years dried, respectively apart from the whiskey lactones; mainly furfural, coniferyl aldehyde and vanillin occurred.

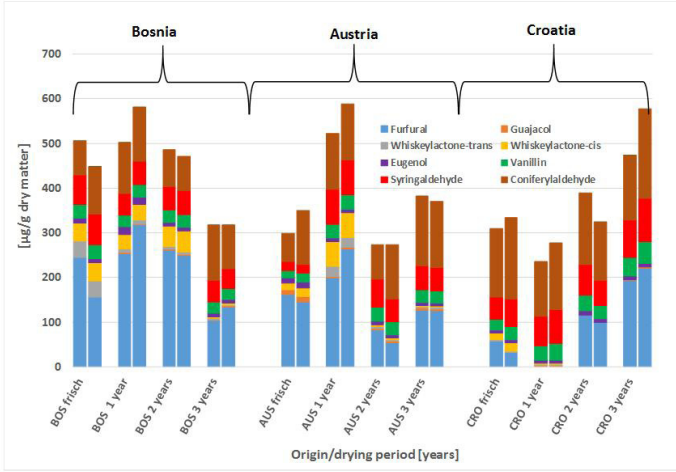

Fig. 1: Comparison of extractives of raw material from all three origins of different drying periods compared to fresh wood with no further treatment (reference).

Fig. 2 shows the 2- and 3-years dried oak samples from all three sources after different toasting treatments. In case of the Bosnia origin, the light and medium toasted samples showed little difference in the total amount of the analyzed extractives.

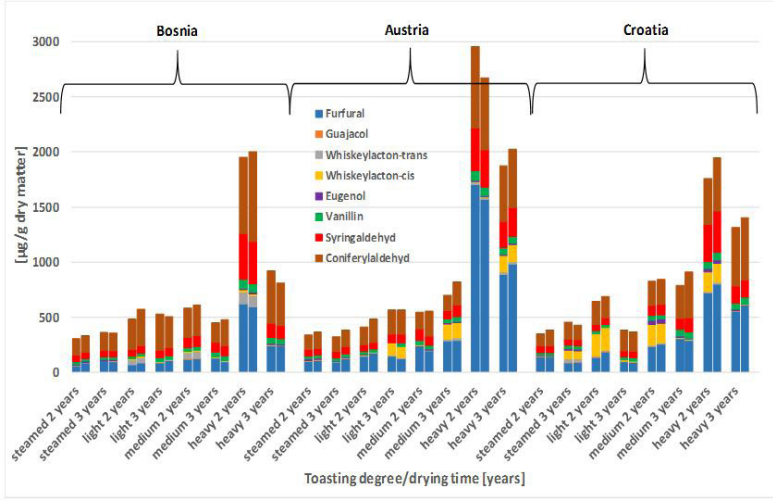

Fig. 2: Comparison of extractives of steamed/differently toasted oak from all three origins after 2 and 3 years drying time, respectively.

In the steamed sample, the total amount of substances was even lower, especially for both whiskey lactones and furfural. In the heavy toasted samples, considerably more furfural, coniferyl aldehyde and syringaldehyde was found, especially for 2- but also for 3-years dried samples. The toasting samples after 2 years of drying were conspicuous for a higher total amount of substances compared to the 3-years dried samples, which may possibly indicate an undesired intense toasting. Interestingly, the ratios of whiskey lactone-cis and -trans had reversed in the 2-year-dried samples after light, medium and heavy toasting compared to the reference (see Fig. 1).

In case of the Austrian origin, only small differences in the total amount of substances were recognized for the steamed samples but also in the light and medium toasted samples. However, the 3-years dried samples showed a 4-times higher amount of whiskey lactone-cis and a 5-times higher amount of whiskey lactone-trans than the 2-years dried samples. In case of the steamed samples, similar to the samples from Bosnia, a lower total amount of substances was found, especially for both whiskey lactones and furfural. In the heavy toasted 2- and 3-years dried samples, similar to those from Bosnia (see Fig. 4), significantly more furfural, coniferyl aldehyde and syringaldehyde was detected. Samples after 2 years of drying and heavy toasting conditions stroke out by their remarkably high total amount of substances, which again can be attributed to a possibly undesired strong toasting. Two-years dried samples from Austria and heavy toasting showed by far the highest amount of extractives.

In case of the origin Croatia, the lowest total amount of extractives was found in the steamed samples after 2 years and the light toasted samples after 3 years of drying. Within the heavy toasted, 2- and 3-years dried samples, similar to those from Bosnia and Austria, considerably more furfural, coniferyl aldehyde and syringaldehyde was found. Two-years dried samples at heavy toasting conditions stroke out due to their very high total amount of extractives, which again can be traced back to unusual toasting conditions. For all three toasting stages, a much higher whiskey lactone-cis concentration was found in 2-years dried samples (180-200 $\mu g \cdot g^{-1}$) than in 3-years dried samples. Interestingly, the 3-years dried and steamed samples from Croatia contained approx. 30 $\mu g \cdot g^{-1}$ whiskey lacton-trans and 70 $\mu g \cdot g^{-1}$ whiskey lacton-cis, although none or only traces of it was found in the reference as well as in the other 3-years dried and toasted samples.

Generally, a high variability in the composition and total amount of extractives was observed in the investigated material. Considerable differences existed in the extractives-profile between the three origins Bosnia, Croatia and Austria. A high degree of variation was also found in the raw material within one respective origin: Long dried wood of Croatian origin led to an increase in the total amount of extractives, however, hardly any whiskey lactones occurred. Here, a high variability was especially found for furfural: Short-dried material contained almost no furfural. To this effect, Austrian material showed less variation: The amount of whiskey lactones in the 1-year dried material was the highest, but decreased sharply with increasing drying time. In the case of the origin Bosnia, the variability was also low for the short drying times and a high content of whiskey lactones was observed for both, fresh and 1- and 2-years dried raw material. Basically, it could be noticed, that the amount of whiskey lactones decreased with the drying time. This may be explained by oxidation processes that occur in the course of drying when compared to fresh wood, leading to a change of substances. Investigations from Schusser et al. (2006), however, showed an increase for both whiskey lactones when comparing fresh and air dried material, but a strong decrease between air dried and chamber dried oak wood.

The total amount of extractives in the raw material from our investigations also varied to a high degree; however, location-dependent differences could also be observed here: Croatian oak displayed the highest extractives amount for the 3-years dried samples. For Austria and

Bosnia, however, the amount was comparable high for the 1-year dried material. In case of fresh material, the extractives content was the highest for the Bosnian origin, which also displayed the highest share of whiskey lactones for all drying periods; this can possibly be associated with the mild, maritime climate in Bosnia. Influences of origin, traced back to differences in climate and soil-composition have also been recognized earlier (Schusser and Schwanninger (2006). When selecting raw material for barrel production, a clear tendency for the use of oak from Bosnian origin shall be considered, especially when whiskey lactones are a quality criterion.

When looking at the further processing of oak wood for barrel production, a strong influence of the toasting procedure on the extractives composition was observed: The amount of whiskey lactones changed with the degree of toasting, and differences were mostly pronounced between medium and heavy toasting. These findings are in concordance with studies from Dumitriu et al. (2017), who have also demonstrated a clearly visible effect between the increasing toasting steps on whiskey lactones in red wine. In case of wood from Croatian and Austrian origin a high amount of whiskey lactones has already been detected after light toasting treatment. The process of steaming did not lead to noticeable advantages regarding the amount and composition of extractives. Our investigations were able to demonstrate, that a medium or light toasting treatment is the optimum treatment for a sufficient yield of whiskey lactones; this confirms the results from Schusser et al. (2006), who proclaimed, that a toasting level between light and medium toasting seems to be interesting for kiln-dried wood with regard to the whiskey lactones. Additional toasting (heavy), though, did not enhance the amount of whiskey lactones; however the total extractive amount increased drastically. This mainly affected those substances with fruit-like and spicy notes (furfural, coniferyl aldehyde, syringaldehyde and vanillin). Investigations carried out in earlier studies (Martinez et al. 1996) were concordant with our findings, as they detected the highest proportion of syringaldehyde/vanillin in samples treated at high temperatures (up to 200°C).

When focusing on the drying process, no clear relationship between the drying period and the content of whiskey lactones could be observed. Although the extractives content for heavy toasting was the highest for all 3 origins, the highest amount of whiskey lactones differed between 3-years (Austria), or 2-years (Croatia and Bosnia) dried samples, respectively.

The results of the project displayed a high variability regarding the relevant primary extractive compounds (polyphenols, whiskey lactones) when comparing different origins and process parameters. Due to the small sample size, an explicit recommendation for an optimal drying time, enabling to maximize the extractives amount, cannot be made. However, a clearly recognizable relationship between the further processing parameters (different degrees of toasting) and the extractives profile is visible: A higher degree of toasting increased the proportions of flavoring substances in wood; especially the whiskey lactones were already being formed at only low toasting degrees, a fact that is of great importance for the cooperage industry.

In general, the variability of the composition of oak wood, together with various drying methods and irregular toasting protocols, can lead to significant, oenologically relevant changes in the flavor profile of barrique wines. For wine producers, the chemical changes which occur in wood during the toasting process are crucial, especially with regard to the increasingly interesting whiskey lactones. The study shows, that besides the importance of the origin, a certain trend in the development of different flavor-bearing substances, can be attributed to the further processing. A possible influence of the "single tree effect" was not investigated due to the limited sample size and should be taken into consideration in further studies as well as the specification of drying parameters (type of drying, weather conditions).

CONCLUSIONS

By careful selection of wood raw material in terms of origin and the respective processing parameters for barrel manufacturing, targeted control of the quality characteristics of barrique stored wine is possible in order to meet the needs of the customer regarding varying wine-tastes. The oenological evaluation shows that the investigated oak wood has a large aroma spectrum and that an "analytical wood selection" can be used for quality assurance, in particular to show the effect of toasting depending on the composition of aromatic compounds. An evaluation of the influence of processing parameters on the wine flavor can be illustrated by targeted experiments. These findings can also be transferred to other wood species such as acacia, cherry, chestnut, ash or mulberry. For the cooperage industry, a robust and practicable method for the selection of oak by origin, duration and drying period as well as the application of a suitable toasting protocol is of great benefit and of great enological interest. On the one hand, the natural resource wood is used more effectively and on the other hand the demands of the cooperage for a consistent wine quality can be met. Aim of the oenology is to increase the fraction of aromatic, desired flavors and to reduce the proportion of bitter and astringent components. Based on the existing data, the decision which of the investigated raw material and processing parameters are most suitable for this purpose cannot be answered right away. Depending on the type of wine to be produced, more or less of the flavors are rated as good or less good in sensory studies. This also applies for the wine matrix (type of bulk-wine or wine-blend), storage, temperature and the way of wine-ageing in the barrel (e. g. oxidative vs. reductive). Further studies with defined wine-types and defined drying and processing parameters will be needed to show the influence of the experimental variants which are useful for the cooperage as a corresponding marketing element.

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