

Extractives Content in Cooperage Oak Wood during Natural Seasoning and Toasting; Influence of Tree Species, Geographic Location, and Single-Tree Effects

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The chemical composition of cooperage oak wood is highly variable, depending upon the tree species (*Quercus robur* L. versus *Quercus petraea* Liebl.), its geographic location, and the single-tree effect. In the process of cask-making, natural seasoning and toasting contribute strongly to the modification of the oak wood chemical composition and therefore influence wine cooperaging. HPLC and GC quantification of ellagitannins and volatile compounds such as whiskey-lactones, eugenol, and vanillin over a sample set of 61 pedunculate oaks and 72 sessile oaks originating from six different forests showed that natural drying leads to a decrease of the ellagitannins and total extractives content level and a quasi constant level of the volatile compounds. Toasting (medium type) drastically enhanced the loss of ellagitannins and the gain in volatile compounds. Statistical treatment showed that the species effect remained significant throughout the process of drying and toasting, but not the provenance. The poor correlation with ring width of extractives levels measured on fresh timber remained unchanged as did the single-tree effect, with high variability found for all chemical parameters. These results provide further evidence that cooperage oak selection should not be based solely on the wood grain or the provenance but rather on a species–provenance combination.

KEYWORDS: Oak; extractives; *Quercus robur*; *Quercus petraea*; seasoning; toasting

INTRODUCTION

Oak wood has always been a material of choice for the construction of barrels. Two species are predominant in France: pedunculate (*Quercus robur* L.) and sessile (*Quercus petraea* Liebl.), respectively covering 1.86 and 2.32 million hectares. In Europe, the barrel industry has based its oak selection on the ring width (grain) and geographic location, that is, on a fine grain (<2 mm) and forests from central France (Tronçais, for example) (1, 2). Consequently, these criteria essentially restrict the source to a specific geographic provenance where silviculture is highly controlled and therefore gives rise to trees with a very fine grain. These forests in France are under the management of the Office National des Forêts.

The oak barrel being not only a container but also a way of wine cooperaging, the chemical composition of oak wood appears to be extremely important. Various studies showed the huge variability that can be found for ellagitannins and volatile compound levels, depending on the species (3–10), the geographic provenance (11–13), the position in the tree, and finally individual trees (3). Regarding the different steps required

for the construction of barrels, the oak wood molecular composition might be altered by natural seasoning and toasting. Natural seasoning, which usually lasts several months, up to two years, is an essential step during which wood loses its humidity and therefore becomes dimensionally stabilized but also undergoes a chemical aging due to rain leaching and biological activity (14). Natural drying induces an important loss of water-soluble compounds; the ellagitannin level decreases during natural seasoning (14), and this loss is predominant over the first three years and on the first few millimeters of each stave face. With regard to volatile compounds, the literature reveals contradictory results; levels of whiskey-lactones, eugenol, and vanillin have been found to increase (11, 15), to decrease (16), or to remain constant during drying. Several assumptions have been proposed to explain such variations (11), but the most important factor in such analyses is the appropriate identification of each piece of wood from the fresh timber to the stave in the barrel.

Toasting is the next step during which a severe wood chemical composition modification is induced. Depending on the degree of toasting, pyrolysis and hydrothermolysis will degrade wood constituents to some extent, not only ellagitannins, which are easily hydrolyzed (17, 18), but also lignins (19) and hemicelluloses will be altered. The degradation of these compounds

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Table 1. Influence of Species and Geographic Location on Chemical Characteristics of Seasoned Wood Samples and Variation with Fresh Wood

| geographic location: species: no. of trees: | 3 locations pedunculate | | 3 locations sessile | | 6 locations | Dordogne 1 | Dordogne 2 | Pyrénées Atlantiques | Cher | Indre et Loire | Saône et Loire |
|---|----------------------------|-----------|------------------------|------------|----------------|-------------------|-------------------|----------------------|---------------|----------------|----------------|
| | 61 | | 72 | | 133 | pedunculate 23 | pedunculate 13 | pedunculate 25 | sessile 24 | sessile 24 | sessile 24 |
| | mean | range | mean | range | % ^c | mean | mean | mean | mean | mean | mean |
| nonvolatile extract (mg/g) | 134.7 | 80–179.6 | 106.8 | 35.6–168.5 | −39.2 | 141.3 | 141.5 | 125 | 113.8 | 100.8 | 105.8 |
| ellagitannins ^a (mg/g) | 48.9 | 25.9–80.7 | 37.4 | 10.1–55.8 | −42 | 51.6 | 51.9 | 45.0 | 41.0 | 30.2 | 40.8 |
| ellagitannins ^b (mg/g) | 46.6 | 30.8–81.1 | 30.8 | 7.3–49.9 | −42.3 | 51.6 | 50.9 | 39.8 | 36.7 | 22.0 | 33.6 |
| ellagic acid (mg/g) | 3.0 | 2.1–3.8 | 2.3 | 0.7–4.3 | −42.9 | 2.9 | 3.2 | 2.9 | 2.4 | 2.3 | 2.3 |
| whiskey-lactones (μg/g) | 1.9 | 0.4–14.4 | 37.1 | 0.8–181.3 | +2.9 | 1.4 | 2.2 | 2.2 | 30.5 | 57.5 | 23.3 |
| <i>cis</i> (%) | 75.8 | | 77.7 | | | 77.2 | 68.7 | 77.9 | 75.6 | 81 | 76.3 |
| <i>trans</i> (%) | 24.2 | | 22.5 | | | 22.8 | 31.3 | 22.1 | 24.4 | 19 | 23.7 |
| eugenol (μg/g) | 1.2 | 0.1–4.5 | 3.3 | 0.3–18.7 | −20.7 | 1.2 | 0.8 | 1.4 | 2.4 | 5.7 | 1.8 |
| vanillin (μg/g) | 10.3 | 2.4–41.4 | 11 | 4.8–32.6 | −21.3 | 11.5 | 8.7 | 10 | 10.3 | 10.8 | 12 |

^a Acid hydrolysis–ellagic acid–HPLC method. ^b Ellagitannin–HPLC method. ^c Percent variation between seasoned and fresh wood.

will contribute to raise the volatile compound level (20). Thus, natural seasoning and toasting will strongly influence the oak wood chemical composition, which in turn will influence wine cooperaging. Many studies have been carried out to compare the influence of species and geographic location of oak wood on wine cooperaging, but these investigations generally focused on one particular aspect of the involvement of oak wood in wine cooperaging. Either fresh, seasoned, or toasted wood as well as cooperaged wine has been analyzed, but no study has addressed the study of wood extractives (3, 7, 10, 11, 13). Moreover, the sample set remained often small, and geographic location and species were sometimes unknown or not mentioned. To study thoroughly the variation of wood chemical composition from fresh timber to wine, a rigorous sampling procedure was applied to a set of 133 trees carefully selected to guarantee at each step of the process identification of the wood pieces (from timber to stave) according to their geographic location and hence their species. In the first part of our work, we studied the influence of single-tree, species, and geographic location on the extractives content of fresh cooperage oak wood (21). The quantification of the eight ellagitannins so far isolated and identified (22–28) and volatile compounds [β -methyl- γ -octalactone, *cis*-(-)-(3*S*,4*S*) and β -methyl- γ -octalactone, *trans*-(+)-(3*S*,4*R*), eugenol, and vanillin], combined with statistical data analysis, revealed the high specificity of oak wood according to the species but a poor correlation with ring width (29). In this continuation of the study, the same chemical parameters have been used in concert with principal component analysis (PCA) and variance analysis on the same tree sample set (133 trees) in order to study the influence of natural drying and toasting on the extractives content and how these results correlate with those obtained on fresh timber.

MATERIALS AND METHODS

Wood Origin, Drying Conditions, and Sample Preparation. The species, geographic location, and physical and chemical characteristics of the 133 trees have already been reported (21). The sample set was constituted from two species (61 pedunculate and 72 sessile trees) from six geographic locations (Dordogne 1 and 2, Pyrénées Atlantiques, Cher, Indre et Loire, and Saône et Loire). The Indre et Loire origin was used as a reference because it is in compliance with cask-maker criteria in terms of species (sessile), grain (fine), and location (central France).

The *dried wood* sampling procedure was as follows: Four staves per tree were selected for the chemical analysis. Staves were not randomly chosen; they were in fact the counterparts of the wood slice quarters that had been used to characterize the fresh wood. These four staves were placed at the same height in the pile to avoid any pile effect on the extraction content. The staves were stored for natural seasoning during 16 months on the Tonnellerie Sylvain site. Prior to

chemical analysis, the selected staves were planed down (1 mm taken off) on each face; a 5 cm long piece was taken at 10 cm from the stave end that was the closest to the fresh wood slice. The whole wood pieces were milled, and the sawn material from the four staves was mixed and sieved in order to keep only the 250 μ m fraction.

The *toasted wood* sampling procedure was as follows: One cask per geographic location (only five, Dordogne 2 had been excluded) was constructed; staves were 24–27 mm thick, and toasting was of medium type conducted over an open oak chip fire. Toasting was conducted at the Sylvain site by only one cask-maker. After cask dismantling, five staves per barrel were randomly sampled for analysis. To measure the toasting influence, analyses were carried out on each face of the staves; the external face not being so much affected by temperature was used as a reference for the toasted one. Therefore, a 20 cm piece was sampled in the middle of the stave, and then a 3 mm thick slice was collected from each stave face.

Nonvolatile Extract, Ellagitannins, Total Phenolics, Free Ellagic Acid, and Volatile Compounds Quantification. Wood sawdust (2–5 g) was extracted with acetone/water (7:3 v/v) for nonvolatile extract and with ethanol/water (7:3 v/v) for the volatile fraction at room temperature for 16 h following the method previously described (21). Ellagitannin acid hydrolysis conditions were those described by Peng et al. (30). Volatile compounds (whiskey-lactone, eugenol, and vanillin) were quantified by gas chromatography according to the internal standard methods using 3-octanol as the reference substance following the method previously described (21).

HPLC analysis of the eight ellagitannins and ellagic acid was performed using an apparatus equipped with a P 4000 gradient pump, an AS 3000 autosampler, a UV 2000 UV detector (ThermoSeparation Products), and a 250 \times 4.6 mm i.d., 5 μ m Lichrospher 100 RP 18 column. The mobile phase was composed of solvent A [$\text{H}_2\text{O}/\text{H}_3\text{PO}_4$ (990:1)] and solvent B [methanol/ H_3PO_4 (990:1)], and gradient elutions of 0–13% B in 30 min and 0–100% in 20 min for ellagitannin and ellagic acid, respectively, were applied at a flow rate of 1 mL/min with detection wavelengths of 280 and 370 nm.

Total phenolics were measured using the Folin–Ciocalteu index method (31). A nonvolatile extract (10 mg) was solubilized in 100 mL of methanol/water (7:3 v/v) and sonicated for a few minutes. To 1 mL of this solution were successively added 50 mL of water, 5 mL of Folin–Ciocalteu reagent (Prolabo), and 20 mL of a 20% sodium carbonate solution, and the volume was made up to 100 mL with water. Reaction took place within 30 min at room temperature. Absorbance was measured at 750 nm with a 1 cm optical path. Calibration was done using a castalagin solution (10 mg of 98% pure castalagin in 100 mL of methanol/water, 7:3 v/v).

Variance analyses and PCA were carried out with SPSS 10.05 software.

RESULTS AND DISCUSSION

Fresh and Seasoned Wood Comparative Analysis. The results of the analysis performed on dry wood samples of the two oak species and the six geographic locations are summarized

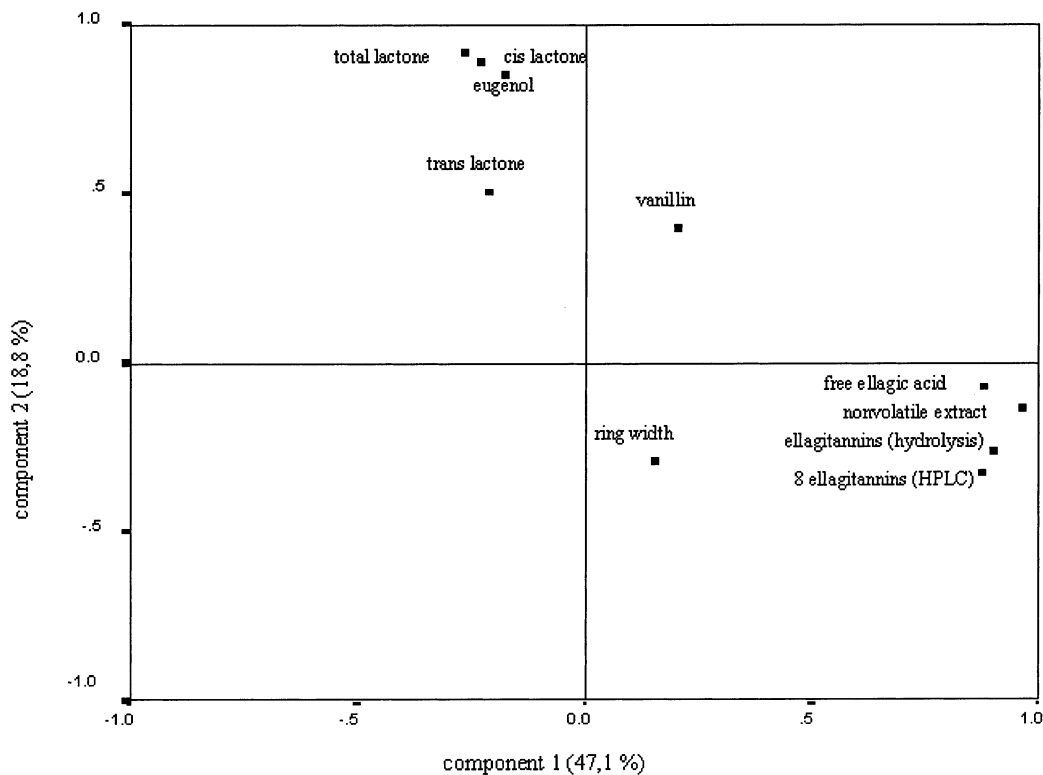


Figure 1. PCA projection of the 10 variables in the 1–2 factorial plan.

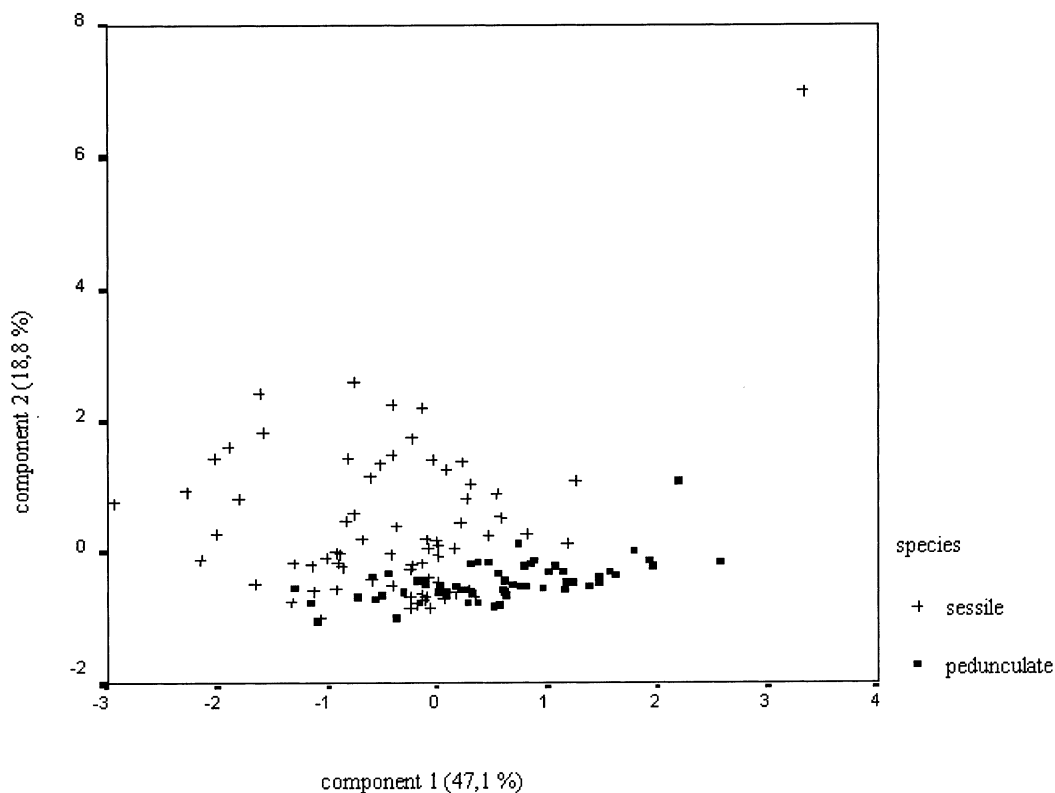


Figure 2. PCA projection of the 133 individuals in the 1–2 factorial plan.

in **Table 1**. These data correlate with those obtained on fresh wood samples (21) and confirm a species discrimination that is based on ellagitannin and whiskey-lactone contents, pedunculate oak having more tannins and fewer volatile compounds than sessile oak.

Variability between single trees was still very high and appeared to be analogous to the variability found for fresh wood.

Variability was high for whiskey-lactones and eugenol and much lower for total nonvolatile extract and the ellagitannin content. Methods validation showed that variability could not be due to experimental errors, for variation coefficients were <5% for all compounds except vanillin (<10%). Such an important variability is tree specific as has already been reported in the literature (32–34). As for fresh wood, PCA analysis showed a

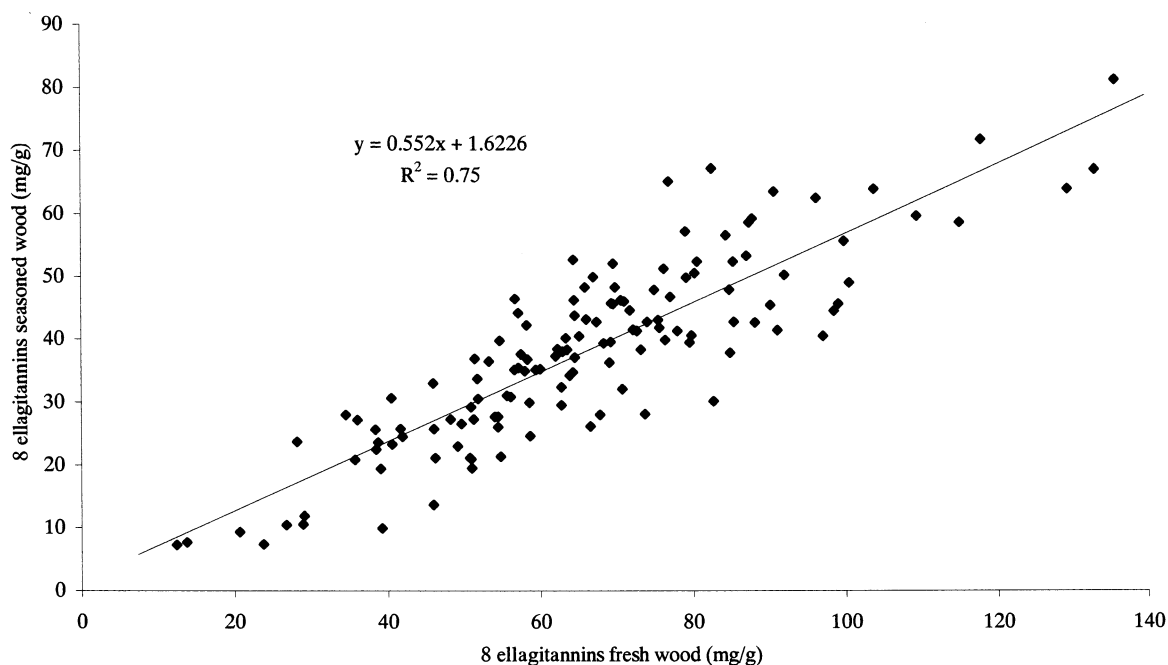


Figure 3. Linear regression of the eight ellagitannins for fresh and seasoned wood ($n = 133$).

Table 2. Comparison of Extractives Content in Seasoned and Toasted Wood

| | pedunculate ($n = 10$) ^c | | | sessile ($n = 10$) ^d | | |
|-----------------------------------|---------------------------------------|---------|-------------|-----------------------------------|---------|-------------|
| | nontoasted | toasted | % variation | nontoasted | toasted | % variation |
| nonvolatile extract (mg/g) | 155.4 | 205.9 | +32.5 | 113.2 | 157.2 | +38.8 |
| total phenolics (mg/g) | 106.3 | 136.9 | +28.8 | 80 | 97.3 | +21.6 |
| ellagitannins ^a (mg/g) | 57.4 | 39.9 | -30.5 | 40.3 | 14.1 | -65.1 |
| ellagitannins ^b (mg/g) | 42.4 | 5.5 | -87.1 | 22.5 | 1.0 | -95.7 |
| ellagic acid (mg/g) | 4.5 | 6.5 | +45.4 | 3.1 | 4.2 | +37.6 |
| lactone (μ g/g) | 0.5 | 1.2 | +148 | 35.1 | 44.7 | +27 |
| eugenol (μ g/g) | 1.6 | 4.6 | +185 | 7.4 | 10.3 | +40 |
| vanillin (μ g/g) | 14.7 | 45.3 | +208 | 14.4 | 48.5 | +237 |

^a Acid hydrolysis-HPLC method. ^b Ellagitannin-HPLC method. ^c $n = 6$ for whiskey-lactone. ^d $n = 15$ for nonvolatile extract, total phenolics, ellagitannins, and ellagic acid.

strong correlation between total lactones, *cis*-lactone, and eugenol and between nonvolatile extract, ellagitannins, and free ellagic acid (Figure 1). These two groups were only slightly correlated to the ring width. Projection of the 133 trees in the 1–2 factorial plan (Figure 2) allows a partial distinction of the two species along component 2, which is related to whiskey-lactones and eugenol contents. The one factor variance analysis over the data indicates that the provenance effect is significant when the species is not taken into account. On the contrary, fewer variables appear to be significant within the same species. These results confirm the trend observed with fresh wood (21).

The results clearly show a significant change in the content of nonvolatile compounds (nonvolatile extract, ellagic compounds) with an average loss of 40% (w/w), whereas changes are less marked for volatile compounds. The decrease of vanillin content (~20% w/w) is nevertheless significant. Slight changes in eugenol content can be noted just above the significance threshold, but whiskey-lactone content remained unchanged. The decrease of ellagitannins can be explained by several processes such as rainwater leaching, microorganism biodegradation, and chemical oxidation (11, 16, 35). With regard to volatile compounds, many factors may influence their concentration during seasoning, particularly when their presence depends on a precursor as is the case for whiskey-lactone (36–38). Level of such compounds may vary greatly according to species and

seasoning conditions. Overall, a fairly high level of correlation was found between fresh and dry wood for most of the parameters. The highest correlations were observed for the nonvolatile extract ($R = 0.9$), ellagitannin content ($R = 0.76$ – 0.89 depending on method), and whiskey-lactone ($R = 0.89$), and the lowest was observed for vanillin ($R = 0.48$). The high level of correlation for ellagitannins is illustrated in Figure 3.

Changes in extractives content, particularly in nonvolatile compounds, were only slightly influenced by single tree, species, and geographic location. Thus, taking the ellagitannin analysis as an example, the decrease of these hydrolyzable polyphenols reaches 40% independently of the tree, its species, and its provenance. Variability in extractives content due to the single-tree effect was maintained throughout drying, as well as the predominant effect of species over provenance. Again, only a slight correlation of ring width with the wood chemical composition criteria was observed.

Seasoned and Toasted Wood Comparative Study. Results of chemical analyses that have been carried out on the two species independently of their provenance are summarized in Table 2. They reveal the drastic changes in wood chemical composition that occur during toasting as reported by other authors (17). Nonvolatile extract and total phenolic contents undergo ~30% increase, and the free ellagic acid content experiences ~40% increase, whereas ellagitannins were strongly

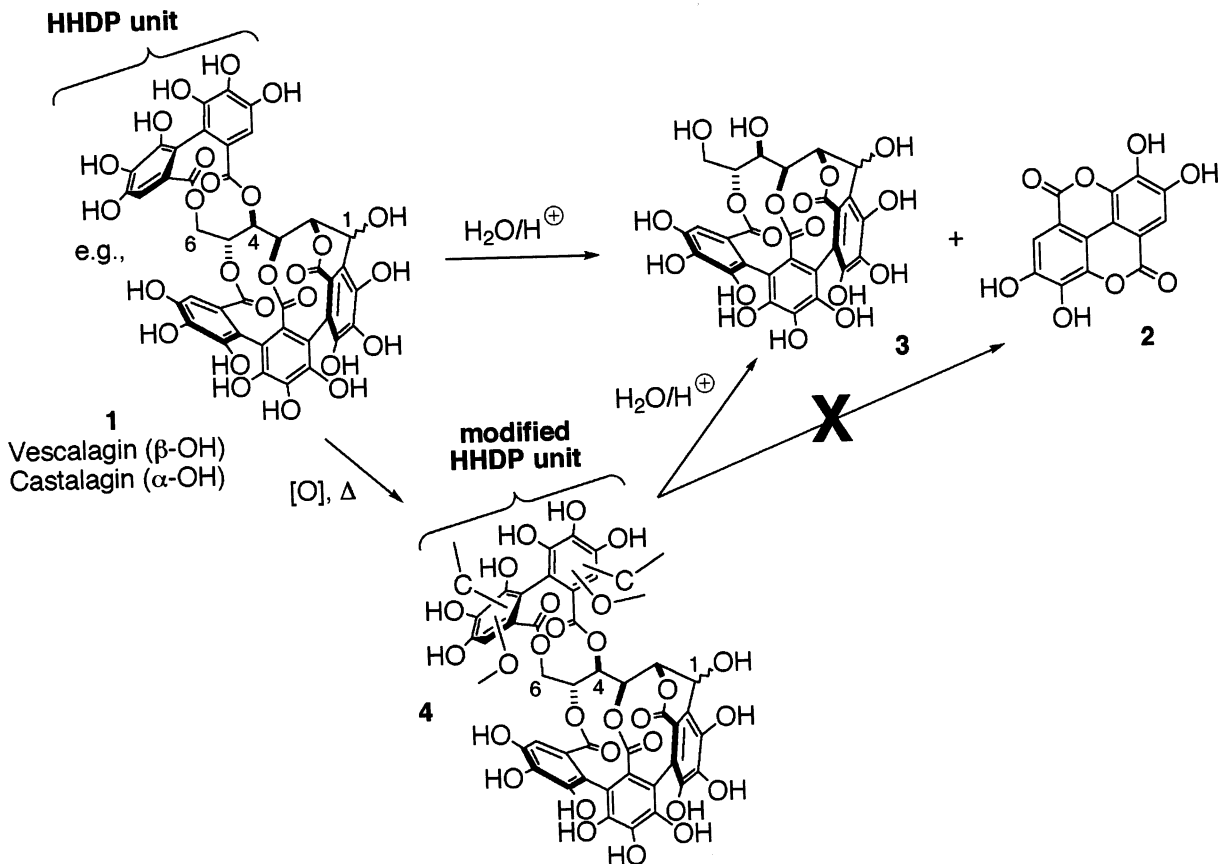
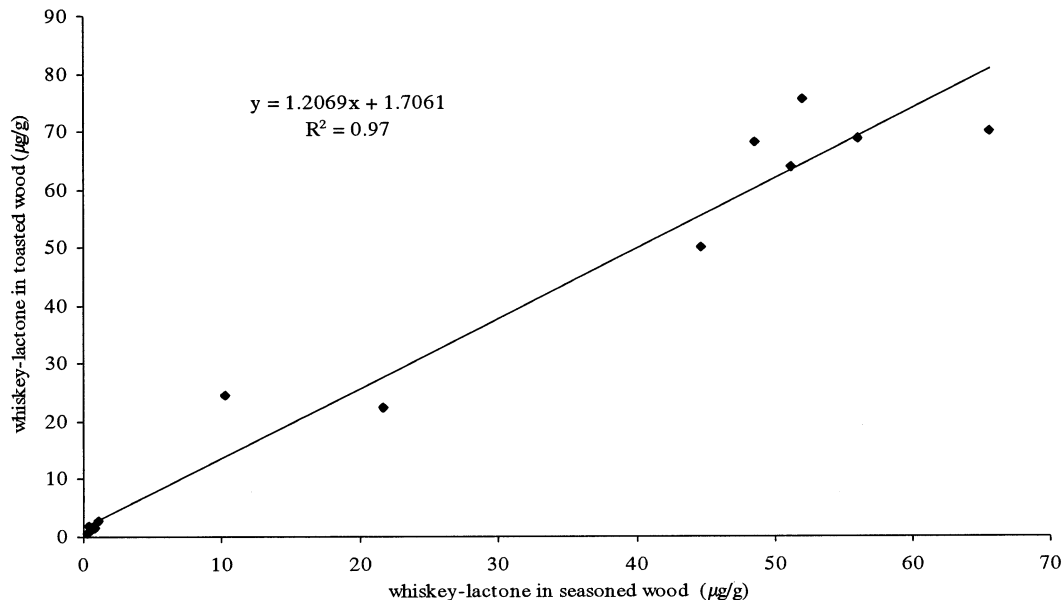


Figure 4. Possible ellagitannin degradation pathways.

Figure 5. Linear regression of the whiskey-lactone for seasoned and toasted wood ($n = 16$).

degraded, with a loss of $>\sim 90\%$ as determined by HPLC analysis of the eight native *C*-glycosidic ellagitannins. Interestingly, corresponding losses of only ca. 30 and 65% were measured by HPLC analysis of ellagic acid released by acid hydrolysis for pedunculate and sessile wood samples, respectively. The fact that the amount of the bislactone released from sessile oak samples is twice that from pedunculate oak samples remains obscure. The 40% increase of free ellagic acid content observed after toasting is far from accounting for the overall disappearance of the eight major ellagitannins as monitored by

HPLC analysis. Thus, ellagic acid does accumulate during wood toasting as a direct result of thermally aided ellagitannin hydrolyses (Figure 4, e.g., $1 \rightarrow 3 + 2$), but this process may not be the only chemical reaction responsible for the actual ellagitannin loss. This apparent dichotomy between the two analyses can be rationalized in several ways. The ellagic acid can either be itself thermolyzed or participate in subsequent coupling reactions with itself or other chemical species. These coupling reactions can, for example, be oxidatively induced during toasting in the presence of oxygen. Following this

scenario, the native ellagitannin structures may also be modified under oxidative conditions in such a way that the release of an intact ellagic acid unit is no longer possible (**Figure 4**, e.g., **1** → **4**) (39). A thermal degradation of **2** does not appear to be an option. A thermogravimetric analysis indicated that this bis-lactone is stable up to 400 °C, but a maximum temperature of only 240 °C is reached at the end of the toasting period. Alternatively, one can also propose that chemical modifications of the native ellagitannin structures involve oxidative C–C and/or C–O phenolic coupling reactions at the 4,6-hexahydroxydiphenyl (HHDP) unit, thus preventing the release of **2** by any chemical means (**Figure 4**). Investigations are currently in progress with the aim of characterizing molecules specifically resulting from the toasting process.

The change in the volatile compounds profile during toasting is opposite that observed for the ellagitannins. A significant increase was measured for the three standard compounds and, particularly, in the case of pedunculate oak samples. These observations find their justification in the various mechanisms that take place during toasting. Hydrothermolysis of lignin explains the rising level of eugenol and vanillin, and the increase of whiskey-lactone can be explained by the generation of precursors (11) and by fatty acids oxidation (40). Again, a high correlation was found for all variables ($R = 0.8$) but one (vanillin) between dry and toasted wood. The highest level of correlation was observed for the whiskey-lactones ($R = 0.98$) as illustrated in **Figure 5** and the lowest for vanillin ($R = 0.38$). This variability of vanillin level in toasted wood can be related to the large difference in vanillin content already expressed in fresh and seasoned wood. This variability is further enhanced during toasting because vanillin, in contrast to eugenol, is a direct product of lignin oxidative degradation. After drying and toasting, which are two critical steps of barrel-making, pedunculate oak staves will always contain less whiskey-lactone than sessile oak ones (**Table 2**). These results confirm species discrimination based on chemical characteristics from the fresh timber to the cask. Toasting does not affect either species chemical specificity or the provenance effect.

The large sample set of trees from two species and different geographical origins allowed us to gather reliable results on variability and correlation of chemical parameters from the fresh timber to the barrel. Both fresh and naturally seasoned sessile and pedunculate oak wood samples exhibit important differences in their extractive contents. Sessile oak is more aromatic, and pedunculate oak is richer in ellagitannins. Statistical treatments of our data indicated that discrimination can be based on species but not on provenance. Furthermore, ring width appeared again to correlate only slightly with extractive contents. This work confirms that selection of cooperage oak wood should be based on a species–provenance combination rather than solely on ring width or provenance. As far as toasting is concerned, the ellagitannin content is drastically modified during this stage of barrel manufacture, and this modification appeared to be species-dependent on the basis of the analysis of the ellagic acid released by acid hydrolysis. The large differences noted in ellagitannin content, as determined by HPLC analysis of either released ellagic acid (**2**) or residual native ellagitannins, suggest that toasting induces chemical reactions after which the hydrolysis of a modified 4,6-HHDP unit cannot release ellagic acid anymore. This observation also reveals the risk of relying exclusively on standard determination of ellagic acid amount to quantify the amount of residual native ellagitannins and their possible chemical modification products. Despite the high level of ellagitannin degradation, species discrimination remains

statistically significant, each species retaining its own chemical criteria of aromaticity and tannicity.

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