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Influence of Wood Barrels Classified by NIRS on the Ellagitannin Content/Composition and on the Organoleptic Properties of Wine

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Supporting Information

ABSTRACT: Ellagitannins are extracted from oak wood during wine aging in oak barrels. This research is based on the NIRS (Oakscan) oak wood classification according to their index polyphenolic (IP) (between 21.07 and 70.15). Their level in wood is very variable (between 5.95 and 32.91 mg/g dry wood) and influenced their concentration in red wine (between 2.30 and 32.56 mg/L after 24 months of aging) and thus their impact on wine organoleptic properties. The results show a good correlation between the NIRS classification and the chemical analysis (HPLC-UV-MS and acidic hydrolysis procedure) and with the wood ellagitannin level, the ellagitannin extraction kinetic, and the ellagitannins evolution in red wine (Cabernet Sauvignon). Moreover, a correlation between the NIRS classification and the increasing intensity of some wood aromas (woody, spicy, vanilla, and smoked/toasted), flavors (bitterness and astringency), and a decreasing intensity of fruitiness was also observed.

KEYWORDS: *ellagitannins, oak wood, red wine aging, tasting, NIRS (near-infrared spectroscopy), astringency, bitterness*

INTRODUCTION

The primary source of tannins in red wine is grape berry seeds and skins,[1,2] which contain proanthocyanidins, also called condensed tannins, in their vacuoles and cell walls.[3] The second most important source of tannins for red wine could be the oak heartwood used to make barrels.[4] During the aging period in oak barrels, red wine in contact with oak wood extracts two families of substances from oak wood; the volatile compounds that encompass aromatic molecules with a low molecular mass such as oak lactone (e.g., *cis*-β-methyl-γ-octalactone and *trans*-*cis*-β-methyl-γ-octalactone) with a coconut flavor; the phenolic aldehydes (e.g., vanillin and syringaldehydes) with a vanilla aroma; the furanic compounds (e.g., furfural and 5-hydroxmethyl-2-furaldehyde) with a sweet caramel flavor; and syringol and guaiacol with a smoky and spicy flavor. The phenolic compounds and especially the ellagitannins are the second group of extractable substances from oak wood. These ellagitannins together with the gallotannins belong to the hydrolyzable tannins family; this term refers to their ability to release ellagic acid under acidic condition.[5,6] Today, over 500 members of these gallic acid-derived polyphenolic natural products have been isolated from various plants and fully characterized.[5,7] The *C*-glycosidic ellagitannins present a structural specificity of having a highly characteristic C−C linkage between the carbon-1 atom of an open-chain glucose core and the carbon-2′ atom of a galloyl-derived unit esterified to the 2-position of the glucose core (Figure 1). This unit is part of a terarylic nonahydroxyterphenoyl (NHTP) unit that is attached at the 2-, 3-, and 5-positions of the glucose core via the ester bonds. Another biarylic unit with the acronym "HHDP" for hexahydroxydiphenoyl is linked on the 4-, and 6-position of the glucose. Castalagin and vescalagin were the first identified and the most abundant ellagitannins in oak wood; they represent between 40 and 60% of the total ellagitannins content in oak wood. Six other ellagitannins have been isolated in *Fagaceous Quercus* and *Castanea* hardwood species, that is, the lyxose/xylose-bearing monomers grandinin and roburin E, the dimers roburins A and D, and the lyxose/xylose-bearing dimers roburins B and C (Figure 1).[8,11]

Recently, some studies on ellagitannin levels and their evolutions in wine have shown that ellagitannin content is an important parameter in wine aging because these highly reactive molecules can react with wine phenolics during wine aging in oak barrels.[9−15] They are involved in several reactions with other wine phenolic constituents, resulting in color stability,[14,16] modulation of astringency (due to their ability to precipitate proteins), modulation of bitterness and roundness of red wine[17] as well as protection of the wine against oxidation.[10,18] They also reveal important biological properties (antioxidant, anticancer, anti-inflammatory, antibacterial, and anti-HIV replication activities).[6,15,19−23]

However, the ellagitannin content in oak wood (*Quercus robur* L. and *Quercus petraea* Liebl.) is influenced by many factors such as ecological factors (soil, climate), age of the tree, topography,[24,25] and the geographic location of the wood piece in the trees[26,27] as well as the processing of wood in cooperage such as the type and duration of drying and toasting.[28] Historically, oak woods were selected by the cooperage industries according to their forest of origin [Tronçais forest

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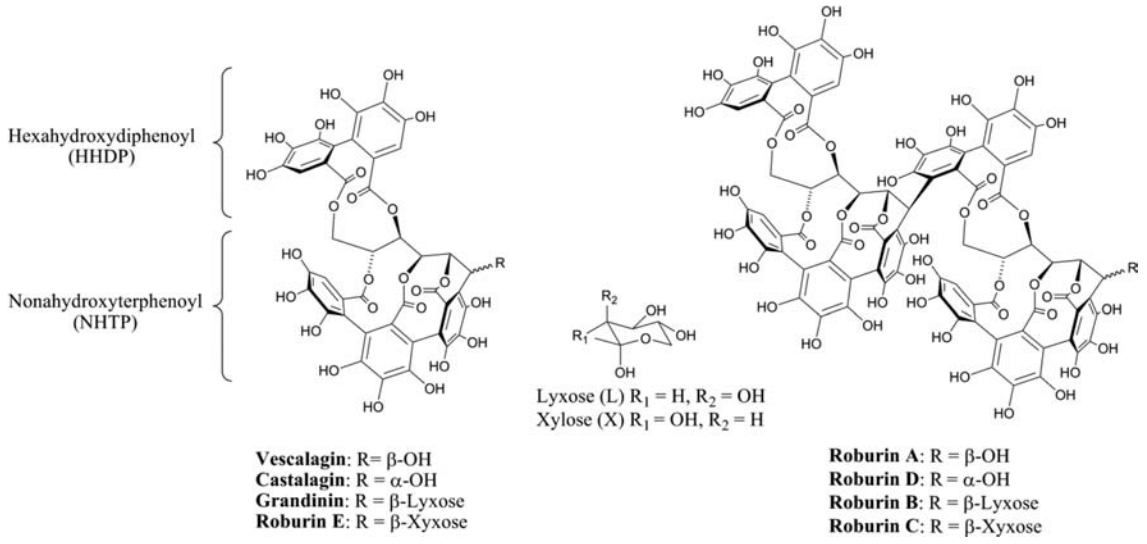

Figure 1. Structures of the main monomeric ellagitannins vescalagin and castalagin as well as grandinin and roburins A–E isolated form *Castanea* (chestnut) and *Quercus* (oak) species.

Table 1. Red Wine Characteristics[a]

Wine Parameters						
total polyphenols (g equiv gallic acid/L)		proanthocyanidins (g/L)	total anthocyanins (mg/L)	polymerized pigments (index)		color intensity (index)
4.08 ± 0.31		3.22 ± 0.59	787.00 ± 26.46	80.57 ± 4.78		1.22
				color contribution (%)		
modified color intensity (index)		shade (index)	yellow (Do 420)	red (Do 520)		mauve (Do 620)
1.39		0.71	36.21	51.15		12.64
Molecular Tannins						
dimer B1 (mg/L)	dimer B3 (mg/L)	catechin (mg/L)	dimer B4 (mg equiv B1/L)	dimer B2 (mg/L)	epicatechin (mg/L)	trimer C1 (mg/L)
7.56 ± 0.19	25.68 ± 0.64	27.91 ± 0.70	4.50 ± 0.11	11.07 ± 0.28	13.54 ± 0.34	4.39 ± 0.11
Molecular Anthocyanins						
Df-3-glc (mg/L)	Cy-3-glc (mg/L)	Pt-3-glc (mg equiv M-3-glc/L)	Pn-3-glc (mg/L)	M-3-glc (mg/L)	Σ glycosylated (mg/L)	
54.62 ± 1.37	3.20 ± 0.08	29.80 ± 0.75	10.31 ± 0.26	171.73 ± 4.29	269.67 ± 6.74	
Pn-3-act (mg equiv Pn-3-glc/L)	M-3-act (mg equiv M-3-glc/L)	Σ acetylated (mg/L)	Pn-3-cm (mg equiv Pn-3-glc/L)	M-3-cm (mg equiv M-3-glc/L)	Σ coumaroylated (mg/L)	
5.31 ± 0.13	70.63 ± 1.77	75.95 ± 1.90	3.42 ± 0.09	21.03 ± 0.53	24.45 ± 0.61	
FOSS Analysis						
CO_2 (mg/L)	density	alcohol level (% vol)	glucose and fructose (g/L)	pH		
502.61 ± 65.64	0.99 ± 0.01	12.92 ± 0.01	0.71 ± 0.04	3.85 ± 0.01		
total acidity (g H_2SO_4/L)	volatile acidity (g H_2SO_4/L)	malic acid (g/L)	lactic acid (g/L)	total polyphenols index		
3.01 ± 0.02	0.15 ± 0.01	0.01 ± 0.01	1.68 ± 0.02	52.71 ± 0.51		

[a]Df-3-glc, delphinidin-3-*O*-glycoside; Cy-3-glc, cyanidin-3-*O*-glycoside; Pt-3-glc, petunidin-3-*O*-glycoside; Pn-3-glc, paeonidin-3-*O*-glycoside; M-3-glc, malvidin-3-*O*-glycoside; Pn-3-act, paeonidin-3-*O*-acetylglycoside; M-3-act, malvidin-3-*O*-acetylglycoside; Pn-3-cm, paeonidin-3-*O*-(*p*-coumaroyl)glycoside; M-3-cm, malvidin-3-*O*-(*p*-coumaroyl) glycoside.

(Allier), Bercé forest (Sarthe), Bertranges forest (Nièvre), Darney forest (Vosges)] and by grain type (i.e., growth ring width). However, this criterion results in important variation in ellagitannin and polyphenol levels.[27] Therefore, to avoid this ellagitannin content variability and to have better control of the organoleptic properties of wines aged in oak barrels, a new apparatus name Oakscan was developed by Radoux cooperage to estimate the ellagitannin concentration in each stave used to make barrels. The Oakscan system uses near-infrared spectroscopy (NIRS) to proceed to this wood classification, a fast and nondestructive procedure.[29] To determine the wood polyphenol index in wood, Oakscan used a regression equation model based on three analyses (absorbance at 280 nm, Folin–Ciocalteu analysis, and ellagitannin level estimated by HPLC) and the wood NIRS spectra.[29]

The aim of this study was, first, to confirm the Oakscan classification[29] in five classes by determination of the ellagitannin level and composition by HPLC-UV-MS in each oak stave used to make barrels. Second, the extraction kinetics of the ellagitannins by French red wine aged in barrels made with the classified staves was investigated during 24 months. Finally, the organoleptic impact on each red wine of the Oakscan classification was evaluated by a trained judge's panel.

MATERIALS AND METHODS

General. Distilled water was obtained from an ELGA system, and Milli-Q (Millipore) water was prepared using a Sarterius-arium 611

system. Methanol (HPLC grade quality, >99.8%) was purchased from VWR (Strasbourg, France). Sodium metabisulfite, ellagic acid, formic acid (>95%), hydrochloric acid (37%), and 1-naphthol (>99%) were purchased from Sigma-Aldrich (St Quentin Fallavier, France). Acetone was purchased from Xilab (Atlantic labo, Bordeaux, France). Evaporations were conducted under reduced pressure at temperatures of <40 °C. Methanol (HPLC grade quality) and Milli-Q (Millipore) water were used for HPLC-UV-MS separations and analyses. Castalagin was extracted from *Quercus robur* heartwood and purified as previously described.[23]

Wood Origin and Drying Conditions. The wood samples were constituted from two oak species (*Quercus robur* and *Quercus petraea*) from the Signy forest (Ardennes), Hagueneau forest (Bas-Rhin), and Gourgeon Lavoncourt forest (Haute-Saône) in France. The raw staves were stored for natural seasoning during 18 months at the Sciage du Berry (Mézières-en-Brenne, France) seasoning park, the Radoux stave mill.

Wood NIRS Classification and Sample Collection. The NIRS apparatus used wavelengths between 800 and 2500 nm for oak wood classification. These wavelengths were collected on the scattered reflection principle, and the background noise was corrected by an external parameter (orthogonalization of partial least-squares regression) thanks to chemometric methods.[30] Before wood was classified with Oakscan, a calibration based on three analyses (absorbance at 280 nm, Folin−Ciocalteu analysis, and ellagitannin level estimated by HPLC) was processed on 400 staves arriving from 33 different batches at the Orléans university (France).[29] Then, the regression equation, obtained by the correlation between these three analyses and the NIRS spectra, was used to determine the wood polyphenol index (IP). The dried wood samples used for chemical analysis were obtained by collecting the ending part of each stave, which was cut during the regular mechanical processing of raw staves just before the NIRS (Oakscan) scanning and classification.[29] The NIRS classification for our study results in five groups according to their polyphenol index (very low potential (VLP) (IP = 21.07 ± 5.45), low potential (LP) (IP = 26.02 ± 5.72), low medium potential (LMP) (IP = 39.03 ± 6.00), high medium potential (HMP) (IP = 55.12 ± 4.89), and high potential (HP) (IP = 70.15 ± 3.09)). Each stave (950 × 27 mm (length × thickness)) classified just by the NIRS system was then assembled in a barrel and submitted to an identical toasting procedure using a traditional method; the temperature level was <280 °C, and the toasting time was 75 min.

Winemaking and Wine Aging. Cabernet Sauvignon grapes were mechanically collected in September 2009 at maturity in the Pessac-Léognan region in France. Then, alcoholic fermentation was carried out at 25 °C in an inox tank (156 hL) with *Saccharomyces cerevisiae* (Actiflore cerevisiae, Laffort) at 11 g/hL followed by maceration during 19 days. Malolactic fermentation was then carried out during 60 days. In December 2009, this Cabernet Sauvignon red wine (Table 1) was aged in duplicate news barrels of 225 L made with the classified oak staves selected as described above. Every month during 24 months, a wine sample (750 mL) was collected in each barrel and stored at 16 °C for the next 5 days until chemical and sensory evaluations. Chemical analyses were conducted on the wine arising from each barrel, whereas for the sensory evaluation, the wines arising from duplicate barrels were assembled (50:50, v/v) before the tasting.

Wood Extraction Procedure. For chemical analysis of the wood, wood samples were first mechanically crushed with a Mill-Retsch bioblock (particle size < 0.6 mm) at room temperature and thereafter stored in the dark prior to processing. An aliquot of the obtained powder (4 g) was extracted using an accelerated extractions system (Dionex ASE 350) with a solvent controller (Dionex Corp., Sunnyvale, CA, USA). The ASE experimental conditions were six extractions by sample with acetone/Milli-Q water (70:30, v/v) solvent, with a static time set at 8 min, a temperature set at 60 °C, and a pressure set at 150 bar. After evaporation under reduced pressure, the obtained residue was redissolved in Milli-Q water and lyophilized to obtain a powder stored in the dark at room temperature.[17]

Red Wine Sample Preparation prior to Ellagitannin Composition Estimation. With an adapted procedure,[31] a red wine sample (120 mL) was loaded on a column (55 mm × 25 mm) that had been packed with TSK HW 50F resin, which had been previously swelled overnight in methanol and equilibrated with H_2O/HCOOH (996:4, 250 mL). After loading 10 mL of the sample on the column, the acidic aqueous solvent (50 mL) was first used to wash out tartaric acid and sugars and, in a second step, an acidic hydro-methanolic solvent (H_2O/MeOH/HCOOH (298:698:4), 100 mL) was used to elute important amounts of the nonellagic polyphenols. Finally, the ellagitannin fraction was eluted using H_2O/acetone/HCOOH (298:698:4, 100 mL). This fraction was evaporated under reduced pressure to furnish a reddish light brown residue, which was dissolved in H_2O/HCOOH (996:4, 1 mL) containing 20 mg/L of chlorogenic acid used as internal standard and filtered (0.45 μm) prior to HPLC-UV-MS analysis.

Total Ellagitannin Concentration Determination in Wood and Wine. The total ellagitannin concentration was determined by the quantification of ellagic acid released during acidic hydrolysis (2 h at 100 °C, 2 N HCl in MeOH)[32] on the one-third of the randomly chosen staves cut, which constitute each barrel, and on each wine.

For the determination of wood total ellagitannin level, the powder (10 mg) was redissolved in 2 mL of MeOH prior to ellagitannin analysis. For the red wine, 50 mL of red wine was evaporated, and the residue was redissolved in MeOH (20 mL). Then, for the determination of the total ellagitannin level, these mixtures were used and placed in three hydrolysis tubes and in two control tubes. After hydrolysis, 100 μL of MeOH containing 1 g/L of 1-naphthol used as an internal standard was added in the hydrolysis tubes and 20 μL in control tubes prior to HPLC-UV-MS analysis. Each triplicate reaction mixture sample and control were analyzed by HPLC-UV-MS using a Thermo Scientific Accela formed by an autosampler (Accela autosampler), a quaternary pump (Accela 600 pump), and a UV−vis detector (Accela PDA), controlled by Xcalibur data treatment system. For analysis, a reverse phase 50 × 2.1 mm, 1.9 μm, Hypersil GOLD column was used. The mobile phases used were composed of solvent A [H_2O/HCOOH (996:4)] and solvent B [MeOH/HCOOH (996:4)], and two different elution gradient were used: 0−35% of B in 1 min, 35−40% of B in 4 min, 40−70% of B in 5 min, 70−80% of B in 6 min, and 80−100% of B in 7 min for wood ellagitannin content analysis; and 0−24% of B in 8 min, 24−30% of B in 13 min, 30−38% of B in 14 min, 38−44% of B in 18 min, and 44−100% of B in 20 min for wine ellagitannin content analysis. The flow rate was set at 0.3 mL/min with detection set at 370 nm to observe the ellagic acid and at 280 nm to observe the 1-naphthol. Ellagic acid and 1-naphthol were separately identified and assigned by comparison of their UV spectra and mass spectra with authentic pure standard. The mass spectra were obtained on a Thermo Scientific MSQ Plus mass spectrometer. Electrospray ionization and mass detection were performed in negative ion mode for the detection of ellagic acid (m/z 301) and in positive mode for the 1-naphthanol (m/z 145) with the following optimized parameters: capillary temperature, 450 °C; capillary voltage, 4.5 V; nebulizer gas flow, 5 L/min; and spray voltage, 50 V.

Determination of Ellagitannin Composition in Wood and Wine. The ellagitannin composition was estimated from the ellagitannin fraction obtained after column fractionation in the case of the red wine, whereas this composition in wood was determined directly from the wood crude extract. The equipment used for this analysis was a Thermo-Finnigan Surveyor HPLC system formed by an autosampler (Surveyor autosampler Plus), a quaternary pump (Surveyor LC pump Plus), and a UV−vis detector (Surveyor PDA Plus) controlled by Xcalibur data treatment system. This HPLC system was also coupled to a Thermo-Finnigan LCQ Advantage spectrometer equipped with an ion trap mass analyzer. The electrospray ionization and mass detection was performed in negative ion mode with the following optimized parameters: capillary temperature, 300 °C; capillary voltage, −46 V; nebulizer gas flow, 1 L/min; desolvation gas flow, 0.25 L/min; and spray voltage, 5 kV. These analyses were carried out in technical duplicates on a 250 × 4.6 mm, 5 μm, Lichrospher 100 RP 18 column. The mobile phases used were solvent A [H_2O/HCOOH (996:4)] and solvent B [MeOH/HCOOH (996:4)] and gradient elution of 0−3% of B in 5 min, 3−

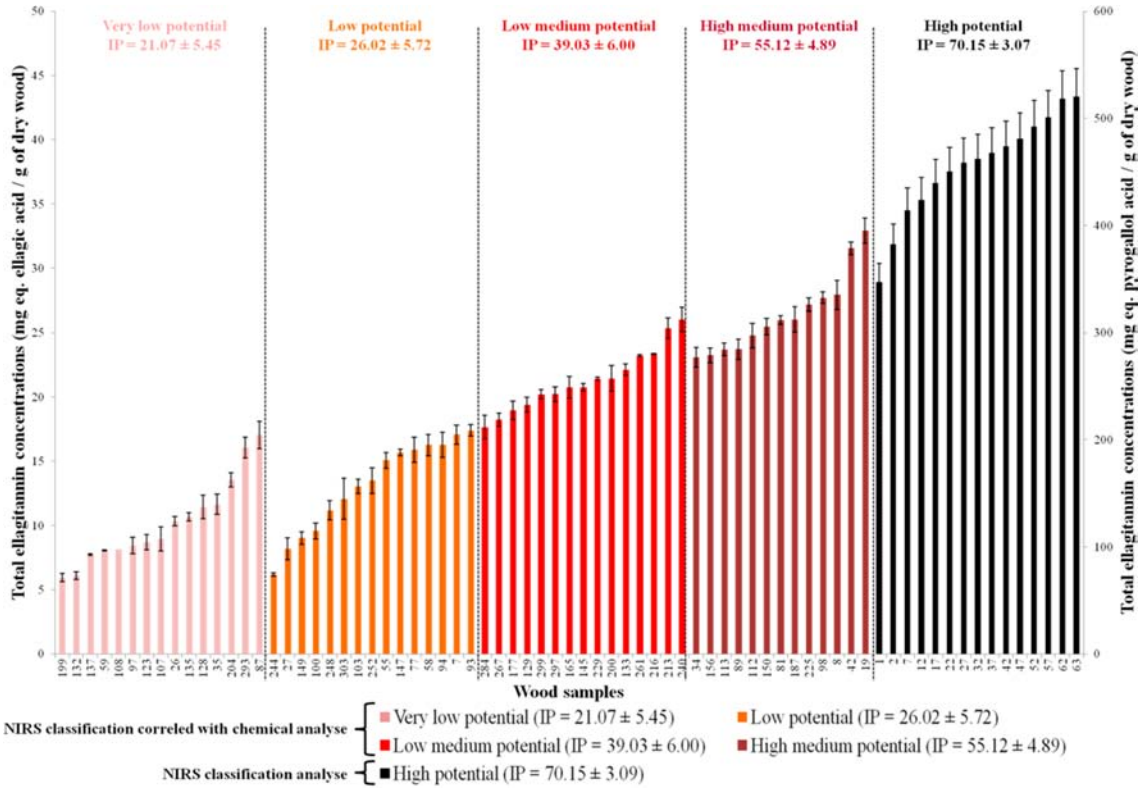

Figure 2. Total ellagitannin concentrations in the wood and correlation with the NIRS oak classification and their IP determined by NIRS. (For detail values, see the Supporting Information.)

20% of B in 20 min, and 20−100% of B in 50 min with a flow rate set at 1 mL/min and a detection wavelength set at 280 nm. Each ellagitannin was separately identified by comparison to their UV spectra and mass spectra according to a previously described procedure.[33] The quantification of each compound was performed using a UV detector at 280 nm in wood extracts or by using their molecular ion for the wine sample. The concentrations of castalagin, vescalagin, grandinin, and roburins A−E were expressed as equivalents of castalagin.

Other Parameters of the Wine. The total proanthocyanidins and total polyphenols were determined by Bate-Smith[34] and Folin−Ciocalteu[35] procedures, respectively. The total anthocyanins were measured by discolorations method using sodium bisulfite ($NaHSO_3$),[36] and the polymerized pigments were determined by discolorations method using sodium metabisulfite ($Na_2S_2O_5$). The color intensity and the other color parameters were analyzed by the Sudraud method[37] on a spectrophotometer at 280, 420, 520, and 620 nm. The concentrations of the flavanols and dimeric and oligomeric proanthocyanins were obtained by using the adapted method[38] on a Thermo-Electron Surveyor HPLC system coupled to a fluorometric detector. The molecular anthocyanins were determined by HPLC with an adapted method described by Burn et al.[39] The alcoholic strength, concentration of CO_2, glucose/fructose sugars, total and volatile acidity, malic and lactic acid, density, pH, and the total polyphenolic index (TPI) were obtained with a Winescan apparatus (FOSS, France).

Sensory Evaluation. Preliminary evaluation of the wines during the aging indicated that differences among the wines were found in taste and in aroma. Consequently, the evaluation was focused on profiling the wine aromas and flavors in the mouth. All sensory analysis were performed with a minimum of 10 trained judges (enologist, wine researcher, and wine salesman) according to ISO 8586-2 (2008), composed of men and women. The formal evaluation consisted of series of five wines, each session being held in the afternoon between 3:00 and 6:00 p.m. The intensities of each descriptor (such as fruity and woody intensity, vanilla, spicy, smoked/toasted, bitterness, astringency, and fruity balance) were rated on a scale from 1 to 7; a score of 1 indicated that a descriptor is not perceived, and a score of 7 indicated a high intensity. The intensity level of each descriptor was then expressed as the mean value of all judges. The samples were presented in randomly coded, clear, INAO 125 mL glasses; distilled water, bread without salt, and neutral cheese were provided for rinsing between wines. All evaluations were conducted in a standard tasting room (norm V 09-105) at 20 ± 1 °C under white lights in separate booths. When a judge had completed the evaluation of a series, those samples were removed and the next was introduced into the booth.

Data Analysis. For the wood and wine data, significant differences were assessed by an analysis of variance (ANOVA). When the ANOVAs were significant ($p < 5\%$), a post hoc test (Newman test) was processed to estimate the effects of ellagitannin concentration on all of the constituents measured in the wines. These statistical analyses were performed using Statistica software (v 10.0.1011.7, StatSoft. Inc., France) for the chemical analysis and correlation, and FIZZ treatment (v2.41B, Biosystemes, Couternon France) for the tasting results. The tasting data were expressed as the arithmetic average for the five tasted wines by the trained judges.

RESULTS AND DISCUSSION

Concentration and Composition of Ellagitannin in the NIRS Classified Staves. The total ellagitannin concentration in the classified oak wood was determined for the VLP, LP, LMP, and HMP groups to confirm the NIRS classification. This procedure is based on the quantification of the ellagic acid released during ellagitannin hydrolysis in acidic media. During this reaction each ellagitannin monomer or dimer released one molecule of ellagic acid. Then, these released ellagic acid concentrations for each classified stave were correlated with the NIRS classification to confirm the accuracy of this non-destructive analysis. A large diversity of ellagitannin concentrations was observed, ranging from 5.95 ± 0.30 to 32.91 ±

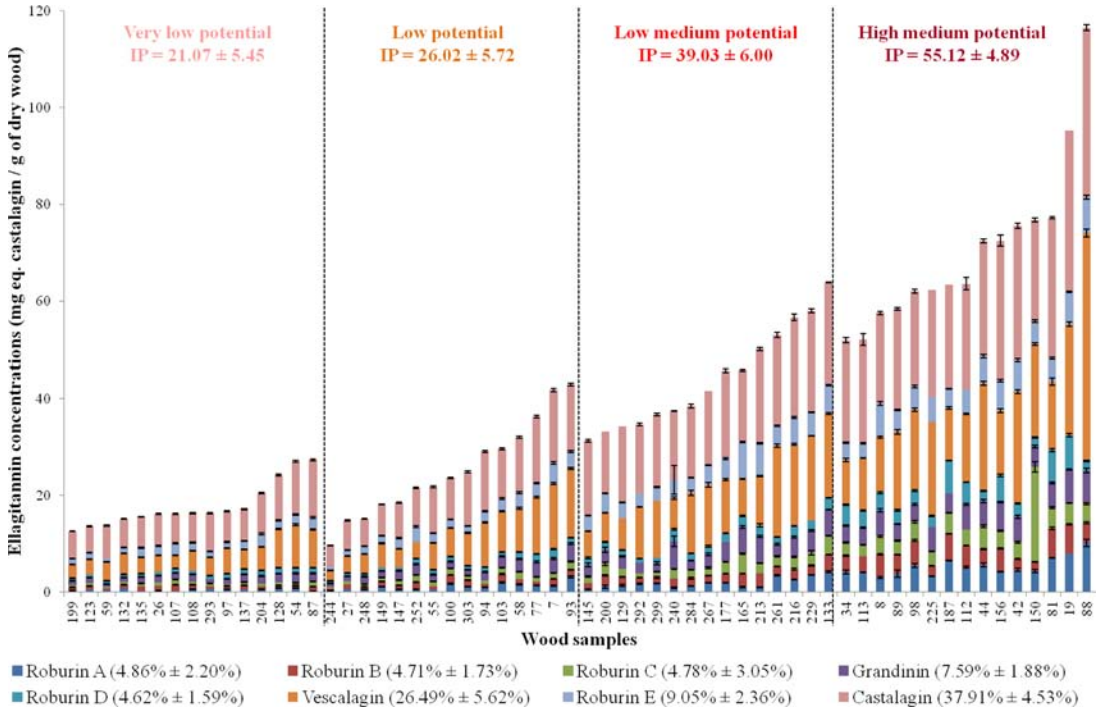

Figure 3. Composition of the eight main ellagitannins and correlation with the NIRS oak classification and their IP determined by NIRS. (For detail values, see the Supporting Information.)

0.98 mg of released ellagic acid per gram of dry wood (Figure 2). These results were expected[11,24] because the ellagitannin concentrations in oak wood depend of the species of oak, the origin of the tree, the rain washing during the staves seasoning, their degradation by micro-organisms, and their chemical oxidation[10,11,15,20,25,26,29,40] as well as the treatment during the processing of wood in cooperage.[4,26,28] It was noted that the total ellagitannin concentrations in classified staves in the VLP group (IP = 21.07 ± 5.45) ranged between 5.95 ± 0.30 and 17.05 ± 1.07 mg of released ellagic acid per gram of dry wood, whereas staves classified in the LP group (IP = 26.02 ± 5.72) showed ellagitannin levels between 6.19 ± 0.13 and 17.39 ± 0.44 mg of released ellagic acid per gram of dry wood, the LMP group (IP = 39.03 ± 6.00) revealed ellagitannin levels between 17.65 ± 0.92 and 26.03 ± 0.95 mg of released ellagic acid per gram of dry wood, and the HMP group (IP = 55.12 ± 4.89) revealed ellagitannin concentrations between 23.09 ± 0.76 and 32.91 ± 0.98 mg of released ellagic acid per gram of dry wood. The high potential group (IP = 70.15 ± 3.09) revealed by NIRS analysis ellagitannin concentrations between 347.01 ± 17.35 and 520.24 ± mg of pyrogallol equivalent per gram of dry wood (Figure 2). These chemical analysis data were highly correlated with the NIRS classification (p < 0.02%). However, small overlapping was observed between the chemical analyses and each NIRS correlated groups. In fact, the NIRS classification and the chemical quantification are indirect analyses, which can induce small differences. Furthermore, the wood, used to make the LP group barrels, was not significantly different from the VLP group (10% > p > 5%). The absence of significant differences between the VLP and LP groups is due to the fact that both groups have a low concentration of ellagitannins and the variation between them was also very small, as well as the fact that global analyses like NIRS have some limitation to precisely quantify such small variation at low level. That is why, today, Radoux cooperage assembled these two groups (VLP and LP) to constitute a unique group.

To have a better overview of the correlation between ellagitannin concentration and NIRS classification, a second method of analysis was employed to confirm the classification on the VLP, LP, LMP, and HMP groups. The eight main ellagitannins were separately quantified by HPLC-UV-MS in each studied stave. As observed with ellagic acid quantification, an important variability between 9.61 ± 0.30 and 95.25 ± 1.34 mg of equiv castalagin per gram of dry wood was observed (Figure 3). In this case, too, a good correlation (p < 0.02%) between the NIRS classification and the sum of each specific ellagitannin concentration quantified by HPLC-UV-MS has been observed. Indeed, the VLP group of staves revealed a sum of each specific ellagitannin concentration ranging from 12.58 ± 0.38 to 27.32 ± 0.79 mg of ellagitannins per gram of dry wood, whereas the LP group of staves ranged from 9.61 ± 0.30 to 42.85 ± 1.36 mg of ellagitannins per gram of dry wood, the LMP group of staves ranged from 31.27 ± 1.15 to 63.85 ± 0.81 mg of ellagitannins per gram of dry wood, and the HMP group of staves ranged between 51.95 ± 1.89 and 116.49 ± 3.51 mg of ellagitannin per gram of dry wood (Figure 3). In this case, too, the LP group was not significantly different from the VLP group (10% > p > 5%). These two chemical methods show that the NIRS classification procedure is an efficient oak wood classification method compared to the traditional method such as species or grain (ring width), which both lead to a high variability of oak extractable compounds such as ellagitannins between barrels.[24,27,41]

The ellagitannin composition in each NIRS classified group revealed that castalagin and vescalagin were always the main ellagitannin and represented, respectively, an average of 38.51 and 25.46% of all the ellagitannins. The average for the other ellagitannins, roburin A, roburin B, roburin C, grandinin, roburin D, and roburin E, are, respectively, 4.86, 4.71, 4.78,

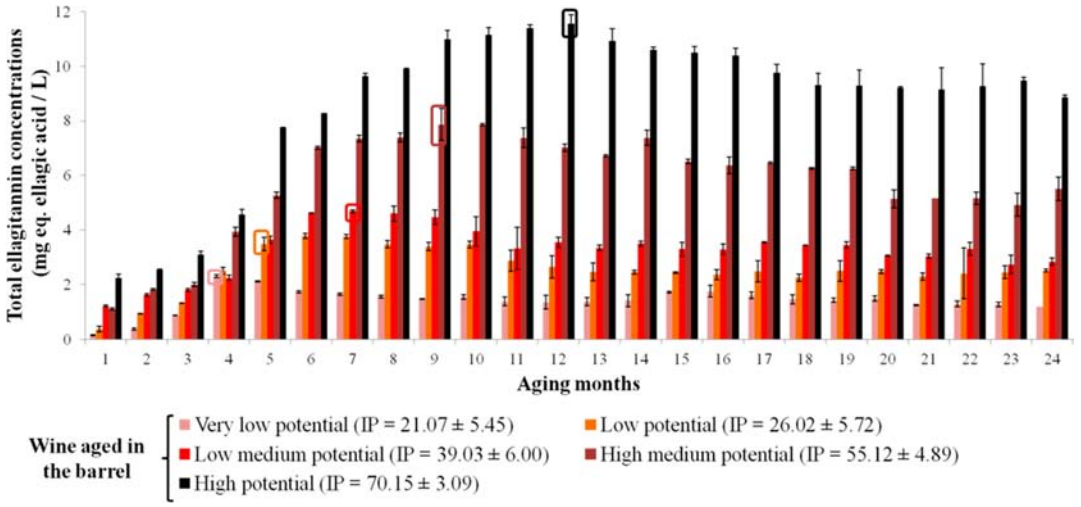

Figure 4. Total ellagitannin concentrations in the same red wine according to their months of aging in contact with the NIRS classified barrels. (For detail values, see the Supporting Information.)

7.59, 4.62, and 9.05% (Figure 3). However, important variations were observed in the ellagitannin compositions in oak wood and were as follows: roburin A (0.69−10.25%), roburin B (2.12−8.77%), roburin C (1.92−8.91%), grandinin (4.61− 15.18%), roburin D (1.70−10.66%), vescalagin (15.73−40.27%), roburin E (5.75−16.81%), and castalagin (30.03−49.50%) (Figure 3). Similar variation in ellagitannin composition has been previously observed.[10,11,17,26,42−44] Furthermore, as expected, these ellagitannin composition variations were not correlated with Oakscan classification because this nondestructive analysis estimated the total amount of each ellagitannins in wood, not each specific molecule.

Concentration and Composition of Ellagitannin in the Red Wine Aged in the NIRS Classified Staves. The first part of this work on the NIRS classification has shown the important variations in the ellagitannin composition of oak wood used in the winemaking process.[45] In the second part, for the first time, the extraction kinetics and evolution of the ellagitannins have been monitored during the aging in the NIRS classified barrels of a Cabernet Sauvignon red wine (Figure 4). Ellagitannins were extracted gradually during wine aging in oak barrels. Indeed, in all the different barrels with different IPs, the ellagitannin concentrations increased in the first months (Figure 4). This result illustrated the slow wine penetration in wood that allows the ellagitannin extraction by this hydroalcoholic solvent. The extraction rates were significantly different between the barrels because, already in the first month, the wine aged in the barrels manufactured with wood having the lowest ellagitannin level present also the lowest ellagitannin concentration (0.15 ± 0.02 mg equiv ellagic acid/L), whereas the same wine aged in the barrels with the highest IP have the highest ellagitannin concentration (2.24 ± 0.15 mg equiv ellagic acid/L) (Figure 4). Thus, the ellagitannin extraction in these first months is directly correlated with wood IP for all of the barrels.

A second part of these results shows, after a few months, a stabilization of this ellagitannin concentration at maximum for all modalities. However, the date and the level of these maxima were very different and correlated (p < 5%) with barrel IP because this maximum of concentration was 2.30 ± 0.05 mg of ellagitannins in equiv ellagic acid/L of wine after 4 aging months for the wine aged in the VLP barrel (IP = 21.07 ± 5.45), 3.48 ± 0.25 mg of ellagitannins in equiv ellagic acid/L of wine after 6 aging months for the wine aged in the LP barrel (IP = 26.02 ± 5.72), 4.62 ± 0.01 mg of ellagitannins in equiv ellagic acid/L of wine after 7 aging months for the wine aged in the LMP barrel (IP = 39.03 ± 6.00), 7.86 ± 0.58 mg of ellagitannins in equiv ellagic acid/L of wine after 9 aging months for the wine aged in the HMP barrel (IP = 55.12 ± 4.89), and 11.56 ± 0.31 mg of ellagitannins in equiv ellagic acid/L of wine after 12 aging months for the wine aged in the HP barrel (IP = 70.15 ± 3.09) (Figure 4). During the first months, the red wine solution extracts the ellagitannins at a rate faster than their evolution rate (oxidation and/or condensation with the wine constituents), resulting in an increase of their concentration. Then, when most of the ellagitannins have been extracted from the first millimeters of the wood, the red wine solution needs to go deeper in the wood to extract more ellagitannins. This moment was dependent on the wood IP.

Thus, the extraction rates decreased and the overall concentration of the ellagitannins remains stable. This stability was longer when the barrel IP increased because the stabilities of the ellagitannin concentration maximum time for VLP barrel, LP barrel, LMP barrel, HMP barrel, and HP barrel were, respectively, 1, 3, 4, 5, and 5 months.

Then, a slight decrease was observed before a new stabilization. These ellagitannin evolutions are again correlated with wood IPs. The time and the percentage of decrease were respectively 36% for 5 months, 35% for 7 months, 29% for 6 months, 19% for 7 months, and 22% for 8 months in wine aging, respectively, in the VLP, LP, LMP, HMP, and HP barrels (Figure 4).

To confirm these results, a second analysis was processed to determine the wine ellagitannin composition (Figure 5). The same trend was found because in all of the wines aged in the different classified barrels, an increased progression in the ellagitannin level was observed in the first months. Then, the wood IP showed a significant influence on the ellagitannin concentration and on the date and level of the ellagitannin maximum principally for the two classes with the highest ellagitannin concentration (p < 5%) (Figure 5D,E). Indeed, these maxima of concentrations were 4.55 ± 0.31 mg of ellagitannins in equiv castalagin/L of wine after 4 aging months (Figure 5A), 11.16 ± 1.74 mg of ellagitannins in equiv

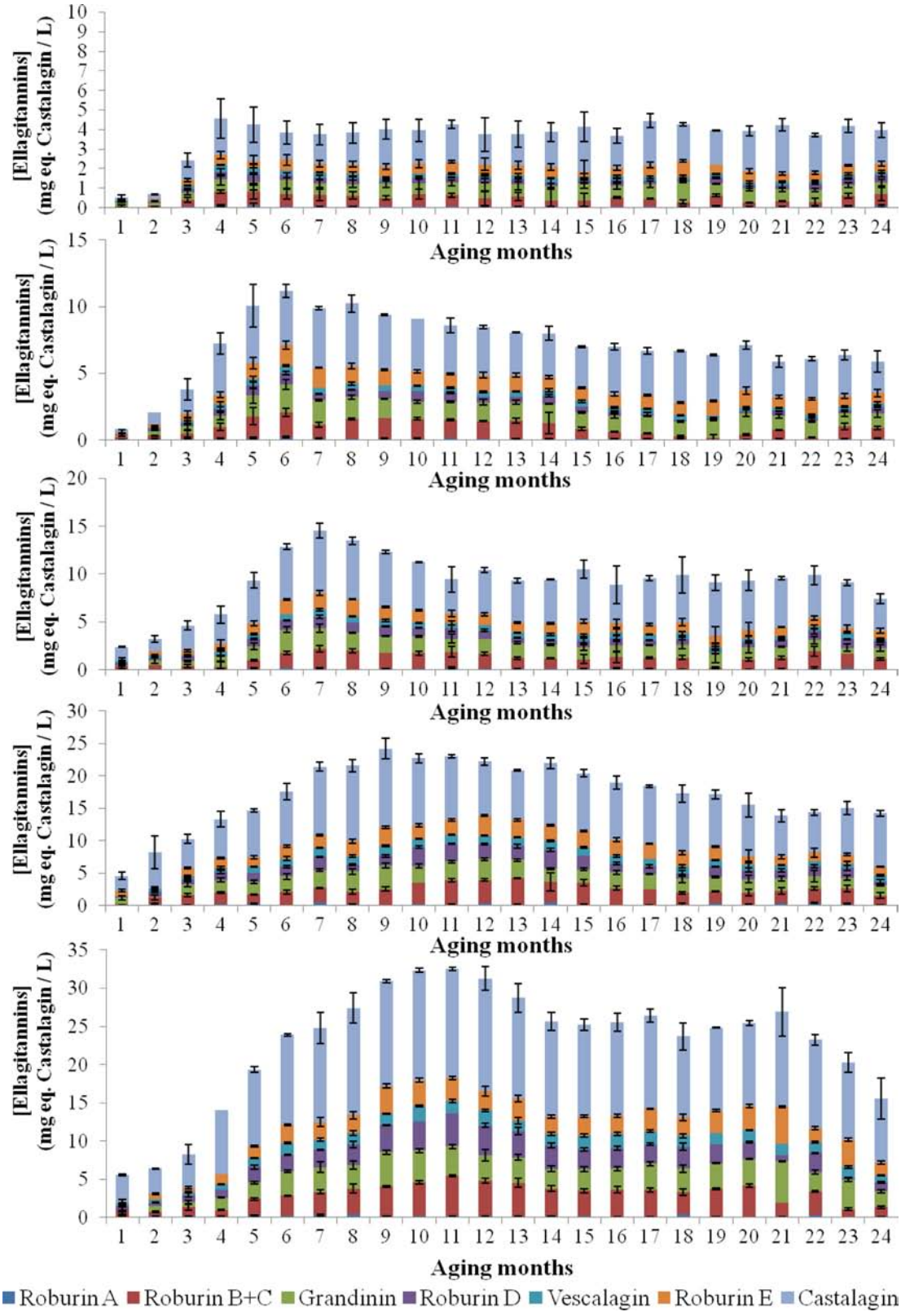

Figure 5. Ellagitannin compositions in red wine according to their months of aging in contact with the NIRS classified barrels: (A) wine aged in a very low potential (VLP) barrel; (B) wine aged in a low potential barrel (LP); (C) wine aged in a low medium potential (LMP) barrel; (D) wine aged in a high medium potential (HMP) barrel; (E) wine aged in a high potential (HP) barrel. (For detail values, see the Supporting Information.)

castalagin/L of wine after 6 aging months (Figure 5B), 14.53 ± 2.13 mg of ellagitannins in equiv castalagin/L of wine after 7 aging months (Figure 5C), 24.20 ± 2.76 mg of ellagitannins in equiv castalagin/L of wine after 9 aging months (Figure 5D), and 32.56 ± 1.09 mg of ellagitannins in equiv castalagin/L of wine after 11 aging months (Figure 5E), respectively, for the VLP, LP, LMP, HMP, and HP barrels (Figure 5). Then, these concentrations decreased slowly due to ellagitannin oxidation

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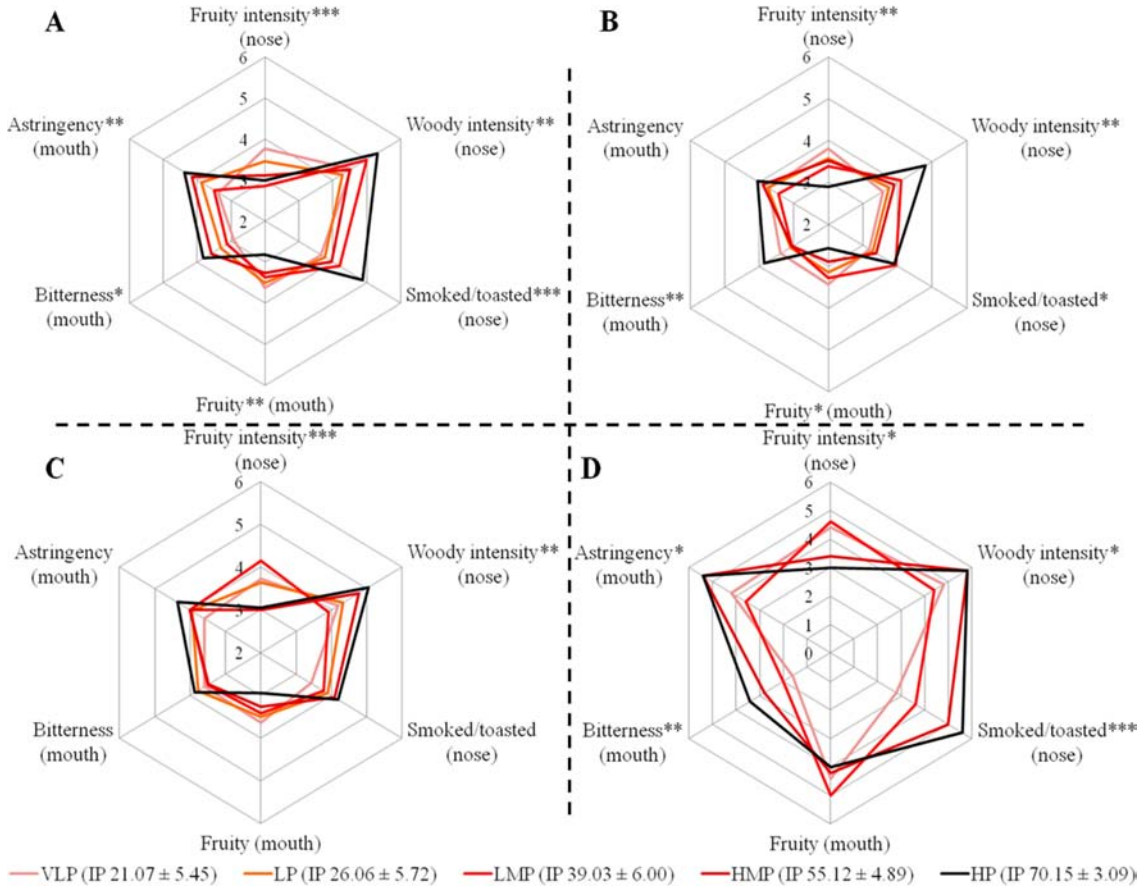

Figure 6. Red wine (Cabernet Sauvignon) tasting results on wine aged in the classified barrels: (A) after 6 months of aging; (B) after 12 months of aging; (C) after 18 months of aging; (D) after 24 months of aging. (*, $p < 5\%$; **, $p < 1\%$; ***, $p < 0.1\%$.)

and/or condensation with the wine constituents.[33] The ellagitannin composition differences between wine and oak wood results of the reactions between wood ellagitannins and wine constituents. Vescalagin and roburin A represent, respectively, 5.48 ± 0.33 and 1.28 ± 0.31% (Figure 5) in the red wine, whereas in the oak staves used to make the barrels, they represent 26.49 ± 5.62 and 4.86 ± 2.20% (Figure 3). The reactions between vescalagin and some wine constituents (i.e., tannins, anthocyanins, and ethanol) have already been studied, and some of the compounds resulting from these reactions have been identified in red wine.[13−15,20,33] Even if the coupling derivatives between roburin A and some wine constituents have not been identified in red wine aged in oak barrels yet, their formation during wine aging in oak barrels is presumed because vescalagin and roburin A exhibit similar configurations at carbon 1, which is the coupling center between ellagitannins and wine constituents (i.e, tannins, anthocyanins, and ethanol).[13,20] Further investigation needs to be carried out to identify such high molecular weight compounds in red wine.

These two analyses describe that a model between the ellagitannin extraction and consumption by red wine aged in barrels and a correlation with the ellagitannin level in wood could be observed. This part of the work shows the importance of Oakscan classification in the ellagitannin extraction kinetics and compositions during wine aging in oak barrels. These differences may result in different organoleptic properties.

Impact of Ellagitannin Concentration in Wood on the Organoleptic Perception of Red Wine. The ellagitannin kinetics study has shown the importance of oak wood classification by Oakscan. The organoleptic impacts were studied by sensory profile tasting at 6, 12, 18, and 24 months of aging. The aroma and flavor of red wine were investigated by trained judges. Descriptors such as fruity and woody intensity, vanilla, spicy, smoked/toasted aromas, fruitiness in the mouth, bitterness, and astringency were influenced by Oakscan classification. First, the aromatic profile of each wine was estimated by the judges. In all of the tastings, the fruitiness and the woody intensity in nose were correlated with wood IP. The woody intensity increased with the wood IP ($p < 5\%$), whereas the fruity aroma and flavor decreased ($p < 5\%$) (Figure 6). This decrease in fruity aroma intensity may be the result of a mask effect of the wood aromas[46] or the consequence of difference in wine aroma evolutions due to modification of the wine oxido-reduction equilibrium as a result of the significant increase of the ellagitannin level in wine. Other wood aromas were correlated with the increased barrel IP as the smoked/toasted aromas ($p < 5\%$). After 24 aging months (Figure 6D), the judges estimated gradually that the spicy aromas increased ($p <$ 0 0.07%) and the vanilla aroma decreased ($p < 3\%$) when the wood IP increase. These effects on the wine aromas were not necessarily expected because the NIRS classification focused only on the wood phenolics. However, even if some aroma concentrations can be correlated with the wood classification, some complementary studies need to be performed on specific wood aroma markers such as aldehyde furanics, whiskey lactone, or vanillin to confirm these hypotheses.

The flavor of wine was also affected by the Oakscan classification. Indeed, the fruitness was judged as less important

($p < 10\%$) at 6, 12, and 18 months in wine when it was aged in a barrel with a wood IP that increased (Figure 6A−C). Moreover, a direct implication of the ellagitannins[18] on the astringency and bitterness intensity ($p < 5\%$) has been observed because these descriptors increased at the same time as the barrel IP; but these impacts in wine were not positively or negatively considered because the judges did not prefer significantly a particular wine.

The important effects of Oakscan classification on the wine organoleptic properties and of a new wood classification method can be assumed from this study. However, a closer look at the wine after 12 or 24 months of aging, which is generally the aging time in oak barrels for red wines before bottling, revealed important differences. After 12 months of aging (Figure 6B), the wine aged in contact with the barrels classified as HP of ellagitannin was described with more intense woody ($p < 0.04\%$), spicy ($p < 10\%$), and smoked/toasted ($p < 2\%$) aromas, bitterness ($p < 0.7\%$) and astringency (tendency) flavors, as well as less intense fruity aromas in the mouth ($p < 1\%$) and in the nose ($p < 3\%$). After 24 months of aging (Figure 6D), a similar trend was also noted by the judges, but the gap between the highest and lowest intensities was higher than at 12 months of aging. This effect was especially noticeable for woody, spicy, and smoked/toasted aromas and bitterness and astringency intensities as well as the lower intensity of fruitiness and vanilla aromas.

In conclusion, the importance of a new classification method for the use of oak wood as barrel has been shown. A good correlation between the ellagitannin concentration determined by acidic hydrolysis or by molecular quantification and the NIRS classification was observed ($p < 0.02\%$). Then, the kinetics and the evolution of the ellagitannins in red wine showed a similar correlation between barrels classified by NIRS procedure and the ellagitannin level found in red wine aged in these classified barrels ($p < 5\%$). Moreover, the ellagitannin extraction kinetics and evolution were influenced by the wood IP with different maximum concentrations and aging time to reach these concentrations ($p < 5\%$). Overall, such correlations revealed that the NIRS oak classification procedure is an efficient technique to classify oak wood according to the ellagitannin level in wood, which is also directly related to the ellagitannin content in red wine aged in contact with the classified oak wood. Furthermore, during the red wine tasting, it appears that the Oakscan classification has a major impact on the wine organoleptic properties in the nose and mouth. Some descriptors (fruity and woody intensity aromas and flavors; vanilla, spicy, and smoked/toasted aromas; bitterness and astringency flavors) were significantly different. As expected, bitterness and astringency were affected by the ellagitannin classification. However, the aroma impacts were not expected. Further investigation needs to be carried out to estimate what oak-derived aromas can follow the same trend as ellagitannin level during NIRS classification. Classifying oak wood prior to barrel realization will allow the winemaker to have better control of the ellagitannin level in their red wine and thus better control of their red wine organoleptic properties.

■ ASSOCIATED CONTENT

Supporting Information

Detailed values of Figures 2−5 on the total and individual concentrations of ellagitannins in each classified oak stave and in the red wine samples during 24 months of aging. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

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