

## Effect of the Seasoning Method on the Chemical Composition of Oak Heartwood to Cooperage

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The effect of various oak wood seasoning methods, natural seasoning in open air, artificial seasoning in a kiln, and a mixed method that combines open air and kiln drying, on the chemical composition in American (*Quercus alba*) and French (*Quercus petraea*) oak was studied. The results confirm the evolution of ellagitannins in wood, low molecular polyphenols, and volatile compounds in relation to oak species and seasoning method. Natural seasoning in open air can be considered a superior method to mixed or artificial drying for wood seasoning in cooperage. It was more effective in reducing the excess of ellagitannins, especially in French oak wood. Moreover, the evolution of wood volatile compounds was more positive in the natural seasoning than mixed or artificial drying, since it led to woods with higher aromatic potential (larger concentrations of compounds such as volatile phenols, phenolic aldehydes, furanic compounds, and *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactones) than mixed or artificial methods. However, the three seasoning methods showed similar effectiveness regarding the desired reduction of off-flavors compounds.

**KEYWORDS:** Volatile compounds; polyphenols; ellagitannins; seasoning; oak wood; *Quercus petraea*; *Quercus alba*

### INTRODUCTION

The process during barrel making in cooperage includes a series of stages that influence the enological quality of the wood, especially seasoning and toasting. Both of these processes decisively affect the structure and final chemical composition of the wood as it is going to be in contact with the wine during its aging. Green wood cannot be used for cooperage since it contains between 40 and 60% humidity and its extractable compounds are not compatible with the objective of improving the quality of the wines.

Wood seasoning in cooperage usually happens under natural conditions in the open air during a variable time period between 18 and 36 months. Seasoning allows reduction of the high percentage of humidity in wood until it is in balance with the ambient humidity. Fiber contraction occurs simultaneously. During this process, oak wood goes through the following phases: dehydration, rehydration, and constant humidity, which slow the process, thus reducing the risk of fissures appearing in the staves. Natural seasoning also results in the wood's maturation, decreasing bitterness and astringency and increasing aromatic properties by means of changes in its chemical

composition. It mainly results in a loss of hydrosoluble polyphenolic substances, such as ellagitannins, which could be due to various physical and chemical mechanisms, including stave leaching by rain (1) and hydrolytic oxidative degradation (2–6), along with fungal enzymatic activity (phenol heterosidase, etherase, and depsidase) (7, 8).

In addition, natural seasoning also has a significant effect on the aromatic profile of wood. During this process, the wood volatile compounds such as lactones, phenolic aldehydes, or volatile phenols show different behaviors; some of them increase their concentrations while others either decrease or show no significant variations. Phenolic aldehydes (vanilline, syringaldehyde, coniferaldehyde, and sinapaldehyde) usually increase their concentrations in wood during natural seasoning, but others, such as eugenol or  $\beta$ -methyl- $\gamma$ -octalactones, show different behaviors, possibly depending on environmental seasoning conditions. All together, however, natural seasoning has a predominantly positive effect on volatile composition and sensorial characteristics of oak wood (2, 9–13).

It is accepted that the best wood seasoning method is that that takes place under natural climatologic and environmental conditions. However, the long immobilization times of the wood in the cooperage seasoning park and the expenses derived from it have aroused interest in other alternative seasoning methods such as final treatments that locate wood by stoves under controlled humidity and temperature conditions or to carrying

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out the complete process artificially. However, some volatile compounds regarded as the most important oak volatiles contributing to the flavor of barrel-aged wines are sensitive to temperature. The isomers, *cis* and *trans*, of  $\beta$ -methyl- $\gamma$ -octalactone, responsible for the characteristic odor of oak, show variable quantities in oak wood depending on the toasting process conditions in cooperage, during which their concentrations may decrease to the extent of being undetectable (14, 15).

The objective of this work was to understand the evolution of oak wood chemical composition, using alternative methods to the natural seasoning, based on thermal treatments of wood in kiln, to reduce its immobilization time in the cooperage. The study includes ellagitannins, low molecular polyphenols, and volatile compounds that are potentially extractable from wood into the wine during aging, contributing to wine taste characteristics and flavor.

## MATERIALS AND METHODS

**Wood Samples.** The oak heartwood used in this work comes from staves of *Quercus petraea* trees grown in Allier (France) and from *Quercus alba* grown in Missouri (EEUU). The staves were subjected to three different seasoning conditions. (i) Natural seasoning: The staves were subjected to climatologic cooperage conditions for a 3 year period (January, 2002–January, 2005) in Magreñan cooperage located in La Rioja, Spain (average annual temperature, 13.9 °C; total precipitation, 380 mm<sup>3</sup>/year; from 2002 to 2005) and were watered daily during the first 2 months and summer and the rest of the time every 15 days, as is normal during the cooperage seasoning process. (ii) Mixed seasoning: The staves were subjected to natural seasoning for the first 18 months and final treatment in a stove for 20 days (temperature, 40 °C; humidity, 70%). (iii) Artificial seasoning: The staves were subjected to treatment in a stove for 40 days (temperature, 40 °C; humidity, 70%).

Wood samples were taken at different times during seasoning, consisting of a minimum of five staves of each geographical origin and seasoning treatment. Different staves were always used for each sampling during seasoning, and they were taken from different positions inside the wood pallets. Several wood pieces were cut out of each stave. The pieces of wood were ground and sieved, taking the sawdust ranging from 0.80 to 0.28 mm.

**Extraction of Phenolic Compounds and High-Performance Liquid Chromatography (HPLC)-Diode Array Detection Analysis.** Wood sawdust samples were extracted with methanol/water, following the method described by Fernández de Simón et al. (16). After removal of the methanol in a rotary evaporator, the aqueous solution was extracted with diethyl ether and ethyl acetate and then freeze-dried. The diethyl ether and ethyl acetate extracts were used for the HPLC quantitative determination of low molecular weight phenolic compounds, and the freeze-dried extract was used for that of ellagitannins. HPLC analysis was carried out with an apparatus equipped with a diode array detector and with a C18 Hypersil ODS (5  $\mu$ m) column (20 cm  $\times$  4 mm i.d.), protected by a precolumn of the same material, according to Cadahía et al. (5, 6). Quantitative determinations were carried out by the external standard method. Roburins B–D were expressed as roburin A equivalents because they are also dimers.

**Extraction of Volatile Compounds and Gas Chromatography–Mass Spectrometry (GC-MS) Analysis.** Volatile compounds were extracted from wood using a hydroalcoholic solution (12% ethanol, 0.7 g/L tartaric acid, and 1.11 g/L potassium bitartrate). After extraction of this with dichloromethane and concentration under nitrogen flux in a Kuderna–Danish apparatus, the organic fraction was used for quantitative determinations, following the method modified by Cadahía et al. (15) from Chatonnet et al. (17). GC-MS analysis of extracts was carried out in a HP 5890 gas chromatograph (Palo Alto, CA), equipped with an HP 5971A selective mass detector and a fused silica capillary column (Supelcowax-10, 30 m  $\times$  0.25 mm i.d. and 0.25  $\mu$ m film thickness) and under the working conditions described in Cadahía et al. (13). Quantitative determinations were carried out by the internal standard method ( $\gamma$ -hexalactone), using peak areas obtained from total ion current (TIC) or selected ion monitoring (SIM), depending on peak purity. The

selected ions *m/z* for the last ones are as follows: guaiacol, 124; 4-methylguaiacol, 138; 4-ethylguaiacol, 137; 4-vinylguaiacol, 135; phenol, 94; eugenol and isoeugenol, 164; syringol, 154; 4-methylsyringol, 168; 4-allylsyringol, 194; 2-furanyl-1-ethanone, 95; butyrolactone, 86; benzaldehyde, 106; benzothiazole, 135; 1*H*-pirrole-2-carboxaldehyde, 95; phenylmethanol, 79; 2-phenylethanol, 91; 2-phenoxyethanol, 94; maltol and isomaltol, 126; furfural, 96; 5-methylfurfural, 110; furfuryl alcohol, 98; 5-hydroxymethylfurfural, 126; *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactone, 99; 1-hexanal and 1-hexanol, 56; 1-nonanal, 57; (*E*)-2-octenal, 70; 2-ethyl-hexanol, 57; (*E*)-2-nonenal, 70; and butoxyethoxyethanol, 57.

**Statistical Analysis.** Univariate analysis was performed using analysis of variance, applying the Student–Newman–Keuls multiple range test. Multivariate canonical discriminant analysis was also carried out with compounds evaluated, using the SAS statistical program (version 6; SAS Institute, Cary, NC).

## RESULTS AND DISCUSSION

The chemical composition of oak heartwood, ellagitannins, low molecular polyphenols, and volatile compounds (Tables 1–4), showed high variations during the seasoning process, in relation to oak species and seasoning method.

**Ellagitannins.** If the results obtained for the ellagitannin evolution during natural, mixed, and artificial seasoning (Table 1) are compared, varying behaviors are observed, according to the wood type and seasoning method. Natural seasoning produced a decrease of the majority ellagitannins (the monomers: castalagin, vescalagin, roburin E, and grandinin) in the two species, American *Q. alba* and French *Q. petraea*, which was significant to the third year. However, the same effect was only witnessed for American wood during the mixed seasoning. The ellagitannin concentration in French wood remained constant when applying the mixed or artificial seasoning and in American wood in the case of artificial seasoning, according to the Student–Newman–Keuls multiple range tests. Similar results in French oak woods were also described by Masson et al. (11), which compared the effect of different drying regimes, two of which combine air drying (natural seasoning) with kiln drying and two which involved only kiln drying. They concluded that the level of ellagitannins either remained constant or declined only slightly during drying, depending on the quantity of free water in the staves and the physical state of the wood. The evolution of ellagitannins during natural seasoning is explained by chemical hydrolysis reactions or enzymatic degradation (7, 8, 18), by oxidative polymerizations (3, 18, 19), and they also can be simply carried away by rainwater in leaching (1). The natural seasoning conditions favor the diffusion process of ellagitannins across the cell wall matrix, hydrolysis and oxidation reactions, and enzymatic degradations, since the wood remains damp for a long time and is subjected to atmospheric oxygen. During kiln drying, only the first pathway is probable (11). It is evident that the mixed and artificial methods studied did not favor these reactions, and consequently, they have been less effective than natural seasoning for the decline of ellagitannins. The increase of ellagitannins in the staves seasoned by means of the mixed method with relation to green wood, observed in French oak, was due mainly to the increase of vescalagin and castalagin proportions (Table 1) and could be attributed to its greater ease of extraction from wood, favored by alterations of bonds with cell wall compounds (11). However, the high variability in ellagitannin contents of French wood has made the increase statistically insignificant.

**Phenolic Aldehydes.** The contents of phenolic aldehydes (Table 2) increased slightly with the three seasoning methods, showing small differences according to wood type. The highest

**Table 1.** HPLC Quantitative Evaluation of Ellagitannins (mg/g of Wood) in Oak Wood Subjected to Different Seasoning Methods<sup>a</sup>

	fresh wood	natural seasoning			mixed	artificial
		1 year	2 years	3 years		
<b>American oak wood</b>						
monomers						
castalagin	5.29 ± 1.80 a	2.91 ± 2.12 ab	2.34 ± 0.32	1.71 ± 0.02 b	1.87 ± 1.20 b	3.03 ± 2.21 ab
vescalagin	2.83 ± 0.64 a	0.69 ± 0.20 b	1.17 ± 0.45	0.44 ± 0.47 b	0.80 ± 0.60 b	1.21 ± 1.07 b
pentosylated monomers						
roburin E	1.38 ± 0.83 a	2.30 ± 2.70 a	0.84 ± 0.12 a	0.51 ± 0.41 a	0.67 ± 0.30 a	1.16 ± 0.74 a
grandinin	2.17 ± 1.05 a	1.81 ± 1.44 a	1.18 ± 0.16 a	1.05 ± 0.61 a	0.73 ± 0.28 a	1.43 ± 0.64 a
dimers						
roburin A	0.70 ± 0.17 a	0.33 ± 0.25 ab	0.34 ± 0.15 ab	0.14 ± 0.18	0.20 ± 0.18 b	0.40 ± 0.35 ab
roburin B	0.65 ± 0.27 a	0.79 ± 0.58 ab	0.23 ± 0.09 a	0.20 ± 0.13 a	0.41 ± 0.14 a	0.57 ± 0.35 ab
pentosylated dimers						
roburin D	0.08 ± 0.05 a	0.08 ± 0.07 a	0.35 ± 0.01 a	0.05 ± 0.02 a	0.02 ± 0.01 a	0.07 ± 0.04 a
roburin C	0.04 ± 0.03 a	0.17 ± 0.01 a	0.01 ± 0.01 a	0.01 ± 0.01 a	0.02 ± 0.01 a	0.07 ± 0.08 a
total	13.15 ± 4.42 a	8.93 ± 7.31 ab	6.14 ± 0.94 ab	4.11 ± 2.82 b	4.72 ± 2.59 b	7.94 ± 5.37 ab
<b>French oak wood</b>						
monomers						
castalagin	10.28 ± 3.96 a	8.19 ± 7.43 a	8.01 ± 4.85 a	3.06 ± 2.21 a	15.91 ± 11.50 a	10.74 ± 6.96 a
vescalagin	4.88 ± 2.05 a	6.99 ± 8.61 a	2.06 ± 0.88 a	1.10 ± 0.95 a	7.24 ± 5.34 a	6.61 ± 8.96 a
pentosylated monomers						
roburin E	3.74 ± 1.14 ab	2.85 ± 1.71 ab	4.47 ± 2.54 ab	1.18 ± 0.91 b	5.82 ± 4.37 a	3.77 ± 1.30 ab
grandinin	4.33 ± 1.01 ab	2.07 ± 0.77 b	4.51 ± 2.11 ab	1.84 ± 0.72 b	5.80 ± 3.21 a	3.49 ± 0.95 ab
dimers						
roburin A	2.04 ± 0.95 ab	1.00 ± 0.71 ab	1.18 ± 0.63 ab	0.49 ± 0.52 b	2.73 ± 1.87 a	1.78 ± 1.41 ab
roburin B	1.40 ± 0.31 ab	0.96 ± 0.45 ab	1.11 ± 0.52 ab	0.38 ± 0.19 b	1.84 ± 1.04 a	1.52 ± 0.60 a
pentosylated dimers						
roburin D	0.17 ± 0.06 ab	0.02 ± 0.01 c	0.11 ± 0.02 bc	0.04 ± 0.02 c	0.21 ± 0.10 a	0.11 ± 0.03 bc
roburin C	0.06 ± 0.04 a	0.14 ± 0.11 a	0.10 ± 0.08 a	0.01 ± 0.02 a	0.22 ± 0.20 a	0.17 ± 0.15 a
total	26.9 ± 9.2 ab	22.2 ± 19.5 ab	21.5 ± 11.0 ab	8.10 ± 5.45 b	34.9 ± 28.9 a	28.2 ± 20.0 ab

<sup>a</sup> Natural seasoning 1, 2, or 3 years, mixed, or artificial seasoning. Average and standard deviation ( $x \pm SD$ ) were calculated for five samples, each one analyzed in duplicate. Different letters in a row denote a significant difference with 95% confidence level in the Student–Newman–Keuls multiple range test.

**Table 2.** HPLC Quantitative Evaluation of Phenolic Aldehydes ( $\mu\text{g/g}$  of Wood) in Oak Wood Subjected to Different Seasoning Methods<sup>a</sup>

	fresh wood	natural seasoning			mixed	artificial
		1 year	2 years	3 years		
<b>American oak wood</b>						
vanillin	9.30 ± 1.90 ab	8.51 ± 2.41 b	12.01 ± 2.21 a	12.36 ± 1.15 a	10.38 ± 1.48 ab	10.41 ± 0.77 ab
syringaldehyde	19.76 ± 3.25 ab	19.27 ± 4.55 ab	19.58 ± 4.32 ab	27.24 ± 8.94 a	15.41 ± 1.34 b	21.61 ± 5.14 ab
coniferylaldehyde	3.21 ± 0.39 c	3.23 ± 0.91 c	4.63 ± 0.63 ab	5.11 ± 0.55 a	3.78 ± 0.53 bc	3.92 ± 0.51 bc
sinapaldehyde	7.60 ± 1.25 a	5.69 ± 2.12 a	10.61 ± 3.07 a	10.33 ± 6.39 a	6.78 ± 1.39 a	7.60 ± 3.04 a
total	7.60 ± 1.25 ab	5.69 ± 2.12 b	10.61 ± 3.07 ab	10.33 ± 6.39 a	6.78 ± 1.40 b	7.60 ± 3.04
<b>French oak wood</b>						
vanillin	7.44 ± 0.59 a	8.51 ± 0.91 a	9.51 ± 0.67 a	8.37 ± 1.40 a	10.31 ± 3.56 a	8.02 ± 1.78 a
syringaldehyde	13.20 ± 1.22 b	15.01 ± 3.13 ab	13.31 ± 1.46 b	15.41 ± 2.17 ab	17.93 ± 3.43 a	12.28 ± 2.51 b
coniferylaldehyde	3.38 ± 0.44 b	4.54 ± 0.68 a	3.41 ± 0.32 b	4.41 ± 0.48 a	4.63 ± 0.78 a	3.20 ± 0.52 b
sinapaldehyde	6.79 ± 0.71 b	8.93 ± 1.62 a	5.92 ± 0.84 bc	6.70 ± 1.61 b	8.64 ± 0.78 a	4.92 ± 0.62 c
total	6.80 ± 0.71 bc	8.93 ± 1.62 b	5.92 ± 0.84 bc	6.70 ± 1.60 bc	8.87 ± 0.85 a	4.92 ± 0.61 c

<sup>a</sup> Natural seasoning 1, 2, or 3 years, mixed, or artificial seasoning. Average and standard deviation ( $x \pm SD$ ) were calculated for five samples, each one analyzed in duplicate. Different letters in a row denote a significant difference with 95% confidence level in the Student–Newman–Keuls multiple range test.

concentrations of phenolic aldehydes highly aromatic like vanillin were obtained in American wood subjected to 2 or 3 years of natural seasoning and in French oak subjected to mixed seasoning or 2 years of natural seasoning, although the differences were not significant because of the high variability shown by fresh woods. The addition of phenolic aldehydes showed statistical differences only between fresh and wood seasoned by mixed method in French oak. Most of the work on wood

seasoning refers to natural seasoning, and they also report either increases in the levels of vanillin (2, 4, 5) or no significant changes during the process (10). On the contrary, Masson et al. (11) have suggested in their study on kiln drying that the level of vanillin decreased, but they were not able to determine the precise behavior of vanillin during this process. The increment of phenolic aldehydes in oak woods during natural seasoning was explained by lignin degradation, by means of a

**Table 3.** GC Quantitative Evaluation of Volatile Phenols ( $\mu\text{g/g}$  of Wood) in Oak Wood Subjected to Different Seasoning Methods<sup>a</sup>

	fresh wood	natural seasoning			mixed	artificial
		1 year	2 years	3 years		
<b>American oak wood</b>						
guaiacol	0.16 ± 0.03 b	0.36 ± 0.26 a	0.14 ± 0.01 b	0.21 ± 0.06 b	0.11 ± 0.02 b	0.15 ± 0.05 b
4-methylguaiacol	0.74 ± 0.23 a	0.47 ± 0.32 ab	0.22 ± 0.04 b	0.35 ± 0.21 ab	0.57 ± 0.25 ab	0.63 ± 0.30 ab
4-ethylguaiacol <sup>b</sup>	0.03 ± 0.01 a	0.07 ± 0.05 a	0.05 ± 0.01 a	0.06 ± 0.04 a	0.03 ± 0.01 a	0.02 ± 0.02 a
4-vinylguaiacol <sup>b</sup>	0.42 ± 0.35 b	1.39 ± 0.89 a	1.84 ± 0.41 a	1.70 ± 0.34 a	0.60 ± 0.11 b	0.72 ± 0.24 b
phenol	0.27 ± 0.09 bc	0.34 ± 0.15 b	0.07 ± 0.02 d	0.53 ± 0.10 a	0.19 ± 0.10 bcd	0.15 ± 0.01 cd
eugenol	22.8 ± 14.7 a	33.0 ± 28.0 a	24.7 ± 24.0 a	30.0 ± 10.2 a	21.9 ± 13.8 a	64.2 ± 45.8 a
isoeugenol	0.71 ± 0.24 a	0.28 ± 0.08 b	0.50 ± 0.06 b	0.42 ± 0.09 b	0.34 ± 0.11 b	0.32 ± 0.12 b
syringol	0.31 ± 0.22 b	1.16 ± 0.47 a	0.77 ± 0.23 a	0.79 ± 0.09 a	0.29 ± 0.15 b	0.32 ± 0.12 b
4-methylsyringol	0.63 ± 0.37 a	0.42 ± 0.12 a	0.66 ± 0.04 a	0.70 ± 0.05 a	0.39 ± 0.15 a	1.17 ± 1.79 a
4-allylsyringol	2.37 ± 1.19 a	0.90 ± 0.32 a	1.38 ± 0.77 a	2.25 ± 1.01 a	0.78 ± 0.73 a	2.53 ± 1.51 a
<b>French oak wood</b>						
guaiacol	0.17 ± 0.12 b	0.10 ± 0.02 b	0.15 ± 0.02 b	1.23 ± 0.71 a	0.09 ± 0.002 b	0.09 ± 0.004 b
4-methylguaiacol	0.81 ± 0.10 a	0.26 ± 0.19 b	0.24 ± 0.04 b	0.19 ± 0.02 b	0.08 ± 0.04 b	0.17 ± 0.12 b
4-ethylguaiacol <sup>b</sup>	0.07 ± 0.06 ab	0.02 ± 0.01 c	0.09 ± 0.03 a	0.04 ± 0.01 bc	0.02 ± 0.002 c	0.02 ± 0.002 c
4-vinylguaiacol <sup>b</sup>	0.82 ± 0.49 b	1.19 ± 0.47 b	2.17 ± 0.53 a	1.98 ± 0.40 a	0.94 ± 0.17 b	0.83 ± 0.14 b
phenol	0.31 ± 0.09 b	0.21 ± 0.03 c	0.11 ± 0.01 d	0.37 ± 0.06 a	0.16 ± 0.02 cd	0.17 ± 0.03 cd
eugenol	13.5 ± 3.9 a	6.14 ± 5.22 a	25.0 ± 11.6 a	22.2 ± 18.9 a	4.86 ± 4.42 a	15.8 ± 31.9 a
isoeugenol	0.62 ± 0.12 ab	0.22 ± 0.08 b	0.89 ± 0.17 a	0.59 ± 0.15 ab	0.90 ± 0.70 a	0.32 ± 0.06 b
syringol	0.62 ± 0.93 a	0.78 ± 0.45 a	0.87 ± 0.26 a	0.97 ± 0.43 a	0.23 ± 0.09 a	0.17 ± 0.05 a
4-methylsyringol	0.98 ± 0.24 a	0.12 ± 0.07 b	0.92 ± 0.24 ab	0.87 ± 0.13 ab	1.25 ± 1.04 a	0.41 ± 0.09 ab
4-allylsyringol	1.43 ± 0.28 a	0.72 ± 0.18 ab	1.45 ± 0.94 a	1.04 ± 0.28 ab	0.73 ± 0.43 ab	0.45 ± 0.24 b

<sup>a</sup> Natural seasoning 1, 2, or 3 years, mixed, or artificial seasoning. <sup>b</sup> Expressed as 4-methylguaiacol. Average and standard deviation ( $x \pm \text{SD}$ ) were calculated for five samples, each one analyzed in duplicate. Different letters in a row denote a significant difference with 95% confidence level in the Student–Newman–Keuls multiple range test.

depolymerization process, and posterior hydrolytic and oxidative degradation of monomers, by either an enzymatic or a chemical process (1, 7, 10), and depends on environmental conditions during seasoning. However, it is accepted that wood heating is the main influence on the phenolic aldehyde levels (20). The studies on the degradation of lignin in oak wood have referred to high temperatures (above 120 °C) used in toasting process in cooperage, in which large increases of phenolic aldehydes from degradation of lignin are obtained.

**Volatile Phenols.** In relation to the evolution of volatile phenols during wood seasoning (Table 3), we find similar behaviors in natural seasoning that were observed in previous experiments (2, 13). The concentrations of some of the aromatic volatile phenols such as guaiacol, 4-vinylguaiacol, syringol, and eugenol increased. The rest of the compounds did not show prominent changes, except 4-methylguaiacol, which decreased during natural seasoning. However, this evolution passed with fluctuations during this natural process. This effect and the high variability shown by these compounds in fresh woods could explain no significant differences in their concentrations at the different steps of wood seasoning. The mixed seasoning method did not produce an effect in the concentration of the majority of these compounds or produced the opposite effect, such as in the case of eugenol, which decreased significantly in French *Q. petraea* wood. Masson et al. (11) suggested a similar decrease in eugenol in wood subjected to kiln drying. Other compounds, like 4-vinylguaiacol, also increased in relation to green wood but in a smaller proportion than what occurred during natural seasoning. Similar wood evolution was observed during artificial seasoning. However, some exceptions must be highlighted. Eugenol levels increased significantly, especially in American wood, which was the opposite to what was observed in the mixed method and according to what appeared under natural conditions, although in this case the increase was greater. These results are important because eugenol concentrations in seasoned woods can determine the aromatic potential of wood during wood–wine interactions, as toasting carried out in cooperage

produces only small variations in eugenol concentrations (14, 15). Volatile compounds may be eliminated from wood by physical or chemical mechanisms (solubilization in water, evaporation, or oxidative degradation process) and are formed at the same time from precursors or lignin degradation. It is possible that one or another mechanism will prevail depending on the method and seasoning conditions.

#### **$\beta$ -Methyl- $\gamma$ -octalactones, Furanic Compounds, Cyclic Ketones, Pyrrole Structures, and Other Volatile Compounds.**

In examining the evolution of volatile compounds shown in Table 4, it is necessary to pay special attention to isomers *cis*- and *trans* of  $\beta$ -methyl- $\gamma$ -octalactone for several reasons: the high aromatic potential (greater for the *cis* isomer than *trans* isomer), the high variability of their concentrations in green oak wood, and the high sensitivity to cooperage toasting. However, their concentrations in wines have reflected those observed in oak prior to toasting (21, 22), so those in wood must be optimized by also adjusting seasoning conditions. Similar to that suggested earlier for French and Spanish oak woods (2, 13), our natural seasoning conditions contributed to the long-term, in French oak wood, formation and slight accumulation of *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactone, after a transitory decrease at 1 and 2 years of seasoning, possibly related to environmental conditions previous to sampling, favoring the leaching, or evaporation of this compound from wood over the formation from precursors (10, 11). A similar tendency was shown in American oak wood, but in this case, the differences among the seasoning steps were not significant, considering the Student–Newman–Keuls's test. On the contrary, mixed and artificial seasoning greatly reduced the contents of  $\beta$ -methyl- $\gamma$ -octalactones, especially the *cis* isomer in French oak wood, in which it was almost completely destroyed (Table 4). The conditions of mixed and artificial seasoning (high temperature and rapid elimination of water) did not favor the formation of these molecules from precursors. For example, the reaction of the formation of  $\beta$ -methyl- $\gamma$ -octalactones from precursors as the glucoside of (3*S*,4*S*)-3-methyl-4-hydroxyoctanoic acid proposed by Wilkinson et al. (23) or the



**Table 4.** GC Quantitative Evaluation of Lactones, Furanic Compounds, Pyranones, and Other Volatile Compounds ( $\mu\text{g/g}$  of Wood) in Oak Wood Subjected to Different Seasoning Methods<sup>a</sup>

	fresh wood	natural seasoning			mixed	artificial
		1 year	2 years	3 years		
American oak wood						
2-furanyl-1-ethanone	0.18 ± 0.05 b	0.64 ± 0.62 a	0.16 ± 0.03 b	0.18 ± 0.04 b	0.07 ± 0.04 b	0.19 ± 0.05 b
butyrolactone	0.33 ± 0.15 a	0.48 ± 0.32 a	0.38 ± 0.07 a	0.30 ± 0.08 a	0.18 ± 0.07 a	0.46 ± 0.52 a
benzaldehyde	0.26 ± 0.05 a	0.23 ± 0.04 ab	0.18 ± 0.08 b	0.12 ± 0.01 c	0.06 ± 0.01 c	0.06 ± 0.01 c
benzothiazole	0.08 ± 0.01 a	0.05 ± 0.03 ab	0.07 ± 0.01 ab	0.02 ± 0.001 b	0.04 ± 0.006 ab	0.07 ± 0.06 ab
1 <i>H</i> -pyrrole-2-carboxaldehyde	0.05 ± 0.03 a	0.02 ± 0.01 bc	0.04 ± 0.02 ab	c	0.01 ± 0.003 c	0.02 ± 0.006 bc
phenylmethanol	1.44 ± 0.17 c	8.69 ± 0.71 a	6.52 ± 2.44 b	1.31 ± 0.13 c	0.22 ± 0.09 c	0.19 ± 0.09 c
2-phenylethanol	0.92 ± 0.38 a	0.81 ± 0.27 a	0.49 ± 0.07 a	0.98 ± 0.32 a	0.57 ± 0.21 a	0.60 ± 0.12 a
2-phenoxyethanol	0.26 ± 0.04 a	0.07 ± 0.02 b	0.02 ± 0.004 c	0.09 ± 0.007 b	0.09 ± 0.07 b	0.11 ± 0.04 b
maltol	0.41 ± 0.15 a	0.38 ± 0.33 a	0.23 ± 0.02 a	0.40 ± 0.05 a	0.23 ± 0.04 a	0.36 ± 0.07 a
isomaltol <sup>b</sup>	0.15 ± 0.01 ab	0.13 ± 0.01 c	0.14 ± 0.001 bc	0.17 ± 0.005 a	0.13 ± 0.003 c	0.16 ± 0.03 a
furfural	3.02 ± 1.53 b	4.03 ± 3.16 b	6.27 ± 6.89 ab	11.53 ± 6.02 a	2.58 ± 1.32 b	5.33 ± 2.98 ab
5-methylfurfural	0.26 ± 0.08 ab	0.30 ± 0.16 ab	0.39 ± 0.14 a	0.43 ± 0.12 a	0.17 ± 0.02 c	0.28 ± 0.08 ab
furfuryl alcohol	0.12 ± 0.07 b	0.08 ± 0.02 b	0.29 ± 0.22 a	0.12 ± 0.08 b	0.10 ± 0.02 b	0.08 ± 0.03 b
5-hydroxymethylfurfural	2.29 ± 1.00 bc	3.08 ± 0.82 bc	2.94 ± 0.97 bc	5.63 ± 1.09 a	1.34 ± 0.15 c	3.28 ± 1.51 b
<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone	4.36 ± 2.88 a	2.77 ± 3.31 a	3.86 ± 0.60 a	4.39 ± 1.46 a	0.78 ± 0.19 a	2.00 ± 1.07 a
<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone	35.6 ± 16.4 a	14.8 ± 14.1 a	27.6 ± 28.4 a	49.2 ± 32.4 a	19.3 ± 13.4 a	19.7 ± 12.1 a
<i>cis/trans</i> ratio	10.4 ± 4.6 a	7.04 ± 2.87 a	8.06 ± 9.63 a	10.6 ± 4.5 a	29.2 ± 25.1 a	11.8 ± 5.6 a
French oak wood						
2-Furanyl-1-ethanone	0.20 ± 0.11 ab	0.29 ± 0.03 a	0.25 ± 0.04 ab	0.14 ± 0.01 b	0.27 ± 0.03 a	0.21 ± 0.070 ab
butyrolactone	0.52 ± 0.27 a	0.22 ± 0.04 bc	0.44 ± 0.13 ab	0.02 ± 0.006 c	0.22 ± 0.04 bc	0.44 ± 0.15 ab
benzaldehyde	0.25 ± 0.07 b	0.14 ± 0.01 c	0.35 ± 0.05 a	0.09 ± 0.01 c	0.09 ± 0.01 c	0.09 ± 0.04 c
benzothiazole	0.08 ± 0.03 ab	0.02 ± 0.01 d	0.09 ± 0.01 a	0.02 ± 0.001 d	0.052 ± 0.008 c	0.06 ± 0.009 bc
1 <i>H</i> -pyrrole-2-carboxaldehyde	0.02 ± 0.01 a	0.02 ± 0.004 ab	0.03 ± 0.01 a	c	0.02 ± 0.005 ab	0.01 ± 0.004 b
phenylmethanol	1.39 ± 0.12 c	5.80 ± 0.49 b	11.20 ± 1.27 a	1.28 ± 0.12 c	0.31 ± 0.10 d	0.30 ± 0.19 d
2-phenylethanol	0.24 ± 0.04 a	0.21 ± 0.03 a	0.66 ± 0.42 a	0.52 ± 0.21 a	0.25 ± 0.09 a	0.71 ± 0.76 a
2-phenoxyethanol	0.11 ± 0.03 bc	0.06 ± 0.03 d	0.03 ± 0.01 d	0.28 ± 0.05 a	0.10 ± 0.02 bc	0.12 ± 0.03 b
maltol	0.42 ± 0.09 a	0.30 ± 0.03 ab	0.39 ± 0.10 a	0.23 ± 0.02 b	0.37 ± 0.09 a	0.33 ± 0.07 ab
isomaltol <sup>b</sup>	0.15 ± 0.01 ab	0.08 ± 0.07 b	0.15 ± 0.007 ab	0.14 ± 0.02 ab	0.16 ± 0.01 a	0.14 ± 0.01 ab
furfural	2.38 ± 0.49 b	2.51 ± 1.09 b	3.49 ± 0.71 b	1.78 ± 0.60 b	6.61 ± 2.51 a	2.44 ± 0.77 b
5-methylfurfural	0.22 ± 0.03 a	0.24 ± 0.08 a	0.27 ± 0.05 a	0.19 ± 0.02 a	0.28 ± 0.01 a	0.19 ± 0.05 a
furfuryl alcohol	0.14 ± 0.08 a	0.11 ± 0.01 a	0.09 ± 0.04 a	0.10 ± 0.04 a	0.09 ± 0.01 a	0.09 ± 0.02 a
5-hydroxymethylfurfural	3.02 ± 1.65 a	2.77 ± 0.67 a	5.24 ± 2.25 a	4.64 ± 3.31 a	4.46 ± 1.26 a	2.86 ± 0.90 a
<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone	9.15 ± 1.54 a	6.58 ± 3.81 a	0.03 ± 0.01 a	11.79 ± 3.70 a	7.33 ± 16.30 a	0.34 ± 0.46 a
<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone	43.9 ± 5.6 a	7.45 ± 6.58 c	0.21 ± 0.10 c	22.1 ± 3.4 b	0.46 ± 0.95 c	3.07 ± 4.30 c
<i>cis/trans</i> ratio	4.88 ± 0.89 b	1.02 ± 0.73 c	8.10 ± 3.22 a	2.14 ± 1.08 bc	2.02 ± 2.23 bc	7.76 ± 2.47 a

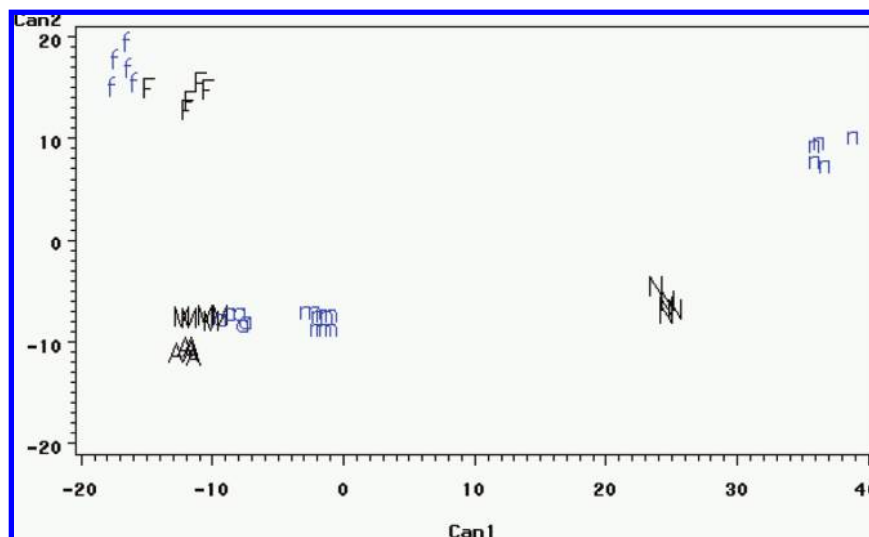
<sup>a</sup> Natural seasoning 1, 2, or 3 years, mixed, or artificial seasoning. <sup>b</sup> Expressed as maltol equivalent. Average and standard deviation ( $\bar{x} \pm \text{SD}$ ) were calculated for five samples, each one analyzed in duplicate. Different letters in a row denote a significant difference with 95% confidence level in the Student–Newman–Keuls's multiple range test.

galloylated glucoside identified by Masson et al. (24) requires highly specific conditions, such as the intervention of an esterase enzyme and an increase in the acidity of the medium. On the other hand, the studies on the degradation of wood lipids to lactones by heat showed contradictory effects, attributed to variations in toasting intensity and method in cooperage (14, 15, 17). At the beginning of toasting, an increase of methyl octalactones contents in superficial wood layer was observed, but when the toasting was prolonged, a total destruction of these compounds took place. Although these studies have referred to high temperatures (above 120 °C) used in the toasting process in cooperage, the lower temperatures over a longer time, used in mixed and artificial seasoning, produced the same effect, the total destruction of methyl octalactones (Table 4).

Referring to the compounds that derive from sugar thermo-degradation, such as furanic compounds, cyclic ketones (furanones and pyranones), pyrrole structures, and related structures (Table 4), the differences among seasoning methods have not been generally significant, due to high variability of the concentrations in fresh wood. However, they show little changes during varying seasoning methods that can contribute to the evolution of the wood aromatic profile. Furanic aldehydes, such as furfural, 5-methylfurfural, and 5-hydroxymethylfurfural, showed different behaviors according to the woods studied.

While their concentrations increased during natural and artificial seasoning in American oak, in French oak, the highest concentrations were obtained during the mixed method. Most of them are especially increased during the cooperage toasting process, so changes in their concentrations according to seasoning method may seem of little enological interest. However, the addition of such changes can contribute to the aromatic potential of wood and they can be indicative of wood positive evolution.

To establish the overall evolution of oak wood aromatic volatile composition during the various seasoning methods, a canonical discriminant analysis was conducted for American and French oaks, taking into account the compounds listed in Table 1–4. The graphic representation on the plane determined by the two main canonical axes (Figure 1) shows groups of points related with different seasoning methods and wood species. The evolution of the phenolic and volatile composition, both for American oak as well as for French oak, has been more evident and positive for the woods subjected to natural seasoning (N and n, in Figure 1) than those subjected to mixed (M and m) or artificial (A and a) conditions. Considering the canonical function 1, which accounted for 68% of the total variance, the statistical distance with respect to the fresh woods was higher for naturally seasoned woods than for those subjected to mixed or artificial seasoning conditions. Discriminant function 1 was



**Figure 1.** Canonical discriminant analysis of phenolic aldehydes (Table 1), volatile phenols (Table 2) *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactones, pyranones (maltol and isomaltol), and furanic aldehydes [furfural, 5-methylfurfural, and 5-hydroxymethylfurfural (Table 3)] from oak woods subjected to natural, mixed, and artificial seasoning (Tables 1 and 2). American and French fresh woods (F and f, respectively). American and French wood subjected to natural seasoning (N and n), to mixed seasoning (M and m), and to artificial seasoning (A and a). Can1 68% and can2 23% of total variance. Eigenvalues for can1 and 2 were 422 and 142, and canonical correlations were 0.998 and 0.996, respectively. Total canonical structure coefficients are shown in Table 5.

**Table 5.** Total Canonical Structure Coefficients for the Main Discriminant Variables in Can 1 and Can 2<sup>a</sup>

	Can 1		Can 2
4-vinylguaiacol	0.8465	phenylmethanol	0.8129
guaiacol	0.6621	benzaldehyde	0.7978
phenol	0.6245	2-phenoxyethanol	0.5692
coniferyl aldehyde	0.5779	<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone	0.4257
5-hydroxymethylfurfural	0.5146	vainillin	-0.4109
syringol	0.5057	4-ethylguaiacol	0.4088
4-methylguaiacol	-0.4862	4-methylguaiacol	0.4082
butyrolactone	-0.4217	<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone	0.3664
phenylmethanol	0.3739	furfural	-0.3617
2-phenoxyethanol	0.3401	coniferyl aldehyde	-0.3234
<i>trans</i> - $\beta$ -methyl- $\gamma$ -octalactone	0.2951	guaiacol	0.2996
benzaldehyde	-0.2799	isoeugenol	0.2845
furfural	0.2631	phenol	0.2797
5-methylfurfural	0.2597	syringol	0.2664
syringic aldehyde	0.2535	syringic aldehyde	-0.2303
maltol	-0.2522	eugenol	-0.2050
sinapic aldehyde	0.1824	5-methylfurfural	-0.1944
vainillin	0.1811	maltol	0.1738
2-phenylethanol	0.1480	4-allylsyringol	0.1227
4-ethylguaiacol	0.1455	isomaltol	-0.1137
<i>cis</i> - $\beta$ -methyl- $\gamma$ -octalactone	0.1258		
isomaltol	0.1120		

<sup>a</sup> The rest of the variables in Can 1 and Can 2 showed coefficients smaller than 0.10.

related, according to the coefficients of total canonical structure (Table 5), mainly to levels of vinylguaiacol, guaiacol, phenol, coniferyl aldehyde hydroxymethylfurfural, syringol, and other compounds with recognized aromatic potential. In addition, other compounds that contributed to the total canonical structure with small coefficients, such as *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactones, must be considered in the discrimination among seasoning methods, because of their high aromatic potential and taking into account the high sensitivity of some of these compounds to cooperage toasting. The canonical coefficients were positives for all of these variables except for 4-methylguaiacol, maltol, butyrolactone, and benzaldehyde that resulted in negatives. This shows an increase of the aromatic potential of wood during natural seasoning. However, the evolution of mixed or artificially seasoned woods was smaller, and it happened down canonical function 2, which accounted for only 23% of the total variance

(Figure 1). In addition, the canonical coefficients resulted in positives (contrary to what was desired) for some compounds with high aromatic potential, such as *cis*- and *trans*- $\beta$ -methyl- $\gamma$ -octalactones, guaiacol and their derivatives, syringol, isoeugenol, maltol, isomaltol, and others (Table 5). This led to woods with smaller aromatic potentials.

**Off-Flavor Volatiles.** Concerning the desired reduction of off-flavor compounds, in relation to disagreeable oak wood aromas, such as sawdust or herbaceous (25), the three seasoning methods showed similar effectiveness. Overall, the concentrations of the studied compounds [1-hexanal, 1-hexanol, 1-nonanal, (*E*)-2-octenal, 2-ethyl-1-hexanol, (*E*)-2-nonenal] decreased in woods independently from applied seasoning method and in greater quantity for French than for American oak woods. The exception was the increase in butoxyethoxyethanol, also similar for the three seasoning methods (Table 6).

**Table 6.** GC Quantitative Evaluation of Off-Flavors ( $\mu\text{g/g}$  of Wood) in Oak Wood Subjected to Different Seasoning Methods<sup>a</sup>

	fresh wood	natural seasoning			mixed	artificial
		1 year	2 years	3 years		
American oak wood						
1-hexanal	0.89 ± 0.39 b	0.64 ± 0.13 b	1.46 ± 0.45 a	0.63 ± 0.14 b	1.01 ± 0.05 b	0.85 ± 0.29 b
1-hexanol	0.23 ± 0.04 a	0.33 ± 0.28 a	0.39 ± 0.07 a	0.49 ± 0.73 a	0.11 ± 0.04 a	0.11 ± 0.05 a
1-nonanal	0.31 ± 0.06 a	0.16 ± 0.02 b	0.14 ± 0.02 b	0.12 ± 0.02 bc	0.09 ± 0.03 cd	0.06 ± 0.008 d
(E)-2-octenal	0.47 ± 0.08 a	0.31 ± 0.08 b	0.36 ± 0.05 b	0.20 ± 0.06 c	0.31 ± 0.03 b	0.26 ± 0.06 bc
2-ethyl-1-hexanol	0.37 ± 0.11 a	0.21 ± 0.04 b	0.16 ± 0.01 bc	0.11 ± 0.01 c	0.12 ± 0.03 bc	0.13 ± 0.02 bc
(E)-2-nonenal	0.48 ± 0.16 a	0.19 ± 0.09 b	0.47 ± 0.05 a	0.29 ± 0.02 b	0.20 ± 0.09 b	0.17 ± 0.04 b
butoxyethoxyethanol	0.21 ± 0.06 de	0.12 ± 0.08 e	0.64 ± 0.03 a	0.29 ± 0.08 cb	0.39 ± 0.12 bc	0.47 ± 0.14 b
French oak wood						
1-hexanal	1.43 ± 0.81 b	1.18 ± 0.24 bc	2.01 ± 0.29 a	0.70 ± 0.21 c	0.64 ± 0.12 c	0.61 ± 0.20 c
1-hexanol	0.15 ± 0.03 bc	0.13 ± 0.04 bc	0.24 ± 0.06 a	0.19 ± 0.04 ab	0.08 ± 0.03 c	0.12 ± 0.03 bc
1-nonanal	0.21 ± 0.06 a	0.19 ± 0.02 a	0.22 ± 0.07 a	0.12 ± 0.01 b	0.03 ± 0.03 c	0.05 ± 0.006 c
(E)-2-octenal	0.55 ± 0.12 a	0.28 ± 0.08 bc	0.38 ± 0.05 b	0.19 ± 0.06 c	0.26 ± 0.05 bc	0.21 ± 0.01 c
2-ethyl-1-hexanol	0.30 ± 0.05 a	0.19 ± 0.04 b	0.17 ± 0.03 bc	0.12 ± 0.01 c	0.16 ± 0.01 bc	0.17 ± 0.04 bc
(E)-2-nonenal	1.22 ± 0.70 a	0.26 ± 0.09 b	0.45 ± 0.08 b	0.25 ± 0.08 b	0.24 ± 0.03 b	0.15 ± 0.04 b
butoxyethoxyethanol	0.17 ± 0.05 cd	0.10 ± 0.005 d	0.73 ± 0.19 a	0.33 ± 0.03 b	0.26 ± 0.04 bc	0.24 ± 0.04 bc

<sup>a</sup> Natural seasoning 1, 2, or 3 years, mixed, or artificial seasoning. Average and standard deviation ( $x \pm \text{SD}$ ) were calculated for five samples, each one analyzed in duplicate. Different letters in a row denote a significant difference with 95% confidence level in the Student–Newman–Keuls multiple range test.

Taking into account the joint overall results, the natural seasoning can be considered a better method than mixed or artificial drying for wood seasoning in cooperage.

Natural seasoning was more effective in reducing the excess of ellagitannins, which are especially desirable in the European oak woods. Concerning the low molecular weight phenols (phenolic aldehydes), no clear disadvantage was observed regarding mixed or artificial methods in relation to the natural method. In addition, these compounds come from lignin degradation and they are formed mainly during the toasting in cooperage so they should not be a high priority for optimization of the seasoning process.

Overall, the evolution of wood volatile composition was more evident and positive in natural seasoning than mixed or artificial drying. Although the differences have not been significant for a lot of volatile compounds when we compare them individually (univariate statistical analysis), the multivariate statistical analysis that takes into account the joint over all volatile compounds and phenolic aldehydes showed an evolution more effective and positive for the woods subjected to natural seasoning than those subjected to mixed or artificial conditions, leading to woods with higher aromatic potentials (higher levels of volatile phenols, phenolic aldehydes, furanic compounds, lactones, and others). However, the three seasoning methods showed a similar effectiveness to the desired reduction of off-flavor compounds such as (E)-2-nonenal.

The known high variation inside the stave lots and the slow and irregular evolution shown by the woods against similar seasoning conditions make evident the advisability of increasing the sample size to clarify and confirm the results obtained. Other works with a larger sample set and also with different wood types and seasoning conditions would need to be carried out, even though they may seem reiterative.

The other designs of the mixed and artificial methods (including artificial wetting and humidity) could possibly improve the reduction of ellagitannins and reproduce the results of natural seasoning, decreasing the prominence of these compounds for optimization of the seasoning process. Wood seasoning in cooperage must allow reduction of the high percentage of humidity and the bitterness and astringency of fresh wood but also must result in the wood's maturation, increasing aromatic properties. Natural seasoning showed better

effectiveness than mixed and artificial methods regarding these desired objectives.

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