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Research Article

Impact of oak barrel aging on furfural formation in industrially produced grape brandy

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Abstract

Brandy is a traditional spirit widely produced in the Balkan region, where industrial production relies on rectification columns and oak barrel maturation to ensure consistent quality. This study investigated the evolution of furfural, a furanic aldehyde, during oak barrel aging of brandy produced from the Vranec grape variety, one of the most important cultivars in North Macedonia. Wines were obtained by controlled fermentation and subjected to double rectification distillation, yielding distillates containing 80–90% (v/v) ethanol. The distillates were diluted to 40% (v/v) ethanol and matured in medium-toast Hungarian oak barrels for 24 months. Furfural was quantified using a spectrophotometric method based on derivatization with an aniline acetate reagent, following preliminary distillation to eliminate color interferences. Measurements were performed at 0, 6, 12, 18, and 24 months of maturation. Fresh distillates already contained measurable furfural concentrations (0.56–1.12 mg.L⁻¹), originating from thermal sugar degradation during distillation. During barrel aging, furfural concentrations increased progressively, reaching 2.12–3.22 mg.L⁻¹ after 12 months. The most pronounced increase occurred between 12 and 18 months (3.44–6.89 mg.L⁻¹). After 24 months, furfural levels stabilized, indicating a balance between extraction from oak wood and secondary reactions. These results suggest that furfural may serve as a useful indicator of maturation progress and sensory development in industrially produced brandy under the conditions investigated.

Keywords brandy, oak barrel maturation, furfural, spectrophotometry

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Introduction

Brandy is a traditional distilled beverage widely produced and consumed in the Balkan region, where product quality is closely associated with maturation in oak barrels. During this process, numerous chemical transformations occur that shape the final sensory profile of the spirit, primarily through extraction of wood derived compounds and subsequent oxidation, esterification, and polymerization reactions, as comprehensively reviewed for oak-aged beverages by [Yoncheva et al. \(2024\)](#), and further discussed by [Wang et al. \(2022\)](#) and [Tarko et al. \(2023\)](#). Among the compounds formed and modified during aging, furfural is considered one of the most significant due to its dual role in aroma development and its relevance to the chemical safety of distilled beverages. It is important to distinguish furfural from 5-hydroxymethylfurfural (HMF), another furanic aldehyde that may occur in alcoholic beverages. While furfural is mainly formed from pentose sugars during oak toasting and is therefore a key marker of wood influence during barrel maturation, HMF originates from the degradation of hexose sugars and is more closely associated with thermal processing and sugar caramelization reactions rather than direct extraction from oak wood ([Morales 2002](#); [Capuano and Fogliano 2011](#)). This distinction is important because HMF is typically linked to heat treatment of raw materials, whereas furfural is strongly associated with wood aging processes in distilled beverages ([Śliwińska et al. 2015](#)).

Furfural (2-furaldehyde; $C_5H_4O_2$) is a heteroaromatic aldehyde belonging to the class of furan derivatives. Its molecular structure consists of a five-membered furan ring bearing an aldehyde functional group at the 2-position. This functional group is chemically reactive and prone to oxidation and condensation reactions, while the furan ring provides aromatic stability but may undergo substitution or degradation under acidic and oxidative conditions ([Singleton 1995](#); [Lee et al. 2001](#)). Furfural is moderately soluble in water and highly soluble in ethanol and other organic solvents, which facilitates its transfer from toasted oak wood into distilled beverages during barrel maturation ([Mosedale 1995](#); [Garde-Cerdán et al. 2002](#)).

Measurable amounts of furfural may already be present in fresh distillates before they are placed in oak barrels. These initial concentrations originate from the thermal degradation of sugars during distillation, where elevated temperatures promote the formation of furanic aldehydes. Even after rectification, trace levels of furfural can remain in the distillate, representing the baseline concentration prior to the influence of oak barrel maturation. The composition of the distillate at this stage is strongly influenced by distillation technology and fractionation control ([Claus and Berglund 2005](#); [Batista and Meirelles 2011](#)).

The major source of furfural during subsequent maturation, however, is the oak wood ([Mosedale 1995](#)). During barrel production, the inner surface of the staves is subjected to controlled heating or toasting, which induces the degradation of pentose sugars present in the hemicellulose fraction of the wood. Through dehydration reactions of sugars such as xylose under elevated temperature and mildly acidic conditions, furfural is formed and retained within the toasted wood structure ([Conner et al. 1993](#); [Chatonnet and Dubourdieu 1998](#)). During storage in barrels, this pre-formed furfural, together with other furanic compounds, is gradually extracted into the brandy under the solvent action of ethanol and the influence of slow oxidative processes ([Tarko et al. 2023](#); [Arduini and Chinnici 2026](#)).

From a sensory perspective, furfural contributes sweet, almond-like, caramel, toasted, and bread-like notes that are characteristic of matured spirits and enhance aromatic complexity ([Puech 1984](#); [Lee et al. 2001](#)). Its concentration is therefore widely considered a marker of wood influence and is closely linked to the degree of barrel toasting and the duration of maturation ([Conner et al. 1993](#); [Wang et al. 2022](#)). In industrial production, especially for brandies obtained using rectification columns, the controlled development of furfural during oak maturation is essential for achieving balanced flavor and product differentiation.

However, furfural also has toxicological relevance in the context of food safety. At elevated concentrations, it has been associated with irritation of the gastrointestinal tract and stress to the liver and kidneys, and has demonstrated carcinogenic potential in experimental animal studies ([Joint](#)

FAO/WHO Expert Committee on Food Additives /JECFA/ 2001). Beyond beverage applications, furfural is widely studied as a bio-based platform chemical derived from lignocellulosic biomass, which highlights both its industrial relevance and the need for monitoring its environmental and health implications (Syguła et al. 2025). Although the levels typically found in matured brandies are far below acute toxic thresholds, continuous monitoring of furfural content remains important for consumer safety and compliance with quality standards.

In the present study, brandy produced from the Vranec grape variety using industrial rectification columns was matured in oak barrels, and furfural content was systematically monitored during 24 months of maturation. Furfural was determined using a spectrophotometric method based on its reaction with aniline acetate reagent, forming a colored complex measured at a specific wavelength. This approach enabled evaluation of furfural dynamics as an indicator of chemical evolution and wood influence during maturation of industrially produced Vranec grape brandy.

Materials and Methods

Wine production and distillation were carried out under controlled industrial conditions at a commercial winery equipped with rectification columns. Chemical analyses were performed in an accredited academic laboratory using validated methods.

Production of Vranec wine for distillation. Wine from the Vranec grape variety (*Vitis vinifera* L.), one of the most important cultivars in North Macedonia and widely recognized for its high yields and frequent use in wine production, was produced as the raw material for distillation. Vinification followed a standard red winemaking procedure (Ribéreau-Gayon et al. 2006). Grapes were destemmed and crushed using a crusher-destemmer. The resulting must be inoculated with the commercial active dry yeast *Saccharomyces cerevisiae* (Sodinal Fermaction Rouge®, Sodinal, France) at a dosage of 20 g.hL⁻¹ to ensure controlled alcoholic fermentation. The must had an initial soluble solids content of approximately 23.0°Brix, pH 3.45, and a total acidity of approximately 6.7 g.L⁻¹, expressed as tartaric acid. Alcoholic

fermentation was carried out in stainless-steel tanks at a controlled temperature of 24 ± 1°C and lasted approximately 9 days until complete sugar depletion. During fermentation, diammonium phosphate (DAP) was added as a yeast nutrient according to the manufacturer's recommendations to support yeast growth and ensure complete fermentation (Ribéreau-Gayon et al. 2006; du Plessis et al. 2002). After completion of alcoholic fermentation, malolactic fermentation proceeded under standard winery conditions until completion.

In total, twelve individual Vranec wines were produced under identical technological conditions, each representing an independent batch with a final volume of approximately 5000 L of wine. The wines were stored separately in stainless-steel tanks under controlled conditions until distillation.

Distillation of Vranec wines. Vranec wines were distilled individually using an industrial Müller copper rectification column (Müller GmbH Brennereianlagen, Oberkirch-Tiergarten, Germany), approximately 20 m in overall height and 1 m in diameter, equipped with 12 perforated sieve trays, electric heating elements, and an automatic temperature-control system. The column design allowed efficient contact between ascending vapors and descending reflux liquid, promoting repeated condensation–vaporization cycles and efficient separation of volatile compounds according to their boiling points and vapor–liquid equilibria (Patil 2023; Yagishita et al. 2025).

The distillation was performed as a continuous rectification process, with each of the twelve wines processed separately under standardized operating conditions. Before processing each batch, the column was allowed to reach steady-state operation. The heating regime was adjusted to maintain the operating temperature between approximately 80 and 90°C, while the wine feed rate, vapor flow, reflux ratio, and fraction-separation procedure were continuously monitored and maintained within the operating specifications of the system. Each of the twelve wines was processed as an individual batch of approximately 5000 L, and the continuous distillation of each batch required approximately 10–12 h to complete.

Operational control of the column enabled selective management of the distillation fractions (Batista and

Meirelles 2011). Particular attention was given to the regulation of temperature gradients, reflux ratio, and vapor flow to ensure efficient separation of undesirable volatile compounds, including low-boiling aldehydes and higher alcohols (fusel alcohols). The initial fractions (heads) were carefully separated to minimize the carryover of undesirable volatile compounds, whereas the heavier congeners (tails) were removed by optimizing the rectification conditions, resulting in a cleaner distillate with improved sensory quality. (Léauté 1990; Mosedale and Puech 1998; Garde-Cerdán et al. 2002).

During the first rectification stage, intermediate distillates containing approximately 60% (v/v) ethanol were continuously collected. These intermediate distillates were subsequently re-distilled in a second rectification step using the same MÜLLER column. During this second distillation, the reflux ratio and fraction-separation parameters were optimized to further increase the ethanol concentration and improve the removal of residual volatile congeners, yielding high-strength distillates containing approximately 86% (v/v) ethanol. The use of rectification columns in brandy production offers higher separation efficiency, reproducible removal of undesirable congeners, and improved standardization of distillate composition compared with conventional pot stills (Claus & Berglund, 2005).

Throughout the production process, identical controlled conditions referred to the use of the same rectification column, operating temperature range, heating regime, wine feed rate, vapor flow, reflux conditions, and standardized fraction-separation procedure for all twelve wines. As a result, each of the twelve Vranec wines yielded an individual distillate with an alcohol content of approximately 86% (v/v) and a final volume of approximately 1000 L, resulting in twelve separate distillates for the subsequent maturation experiment. The distillates were transferred to individually labeled stainless-steel tanks and stored under controlled conditions until the beginning of the maturation process.

Dilution and maturation in oak barrels. The high-strength distillates obtained from each of the twelve individual Vranec wines (approximately 1,000 L per distillate, 85–90% (v/v) ethanol) were diluted to a commercial alcohol strength of approximately

40% (v/v) using softened water with low mineral content and an electrical conductivity of approximately $10 \mu\text{S}\cdot\text{cm}^{-1}$. The use of softened water minimized the risk of mineral-induced turbidity and ensured the chemical stability of the distillates prior to maturation. After dilution, each distillate was stored separately in stainless-steel tanks until transfer into oak barrels.

From each of the twelve diluted distillates, a representative portion was transferred into a separate new medium-toast Hungarian oak barrel (225 L; HM+T, Hungary), resulting in a total of twelve individual barrels corresponding to samples B1-B12. The barrels had not previously been used for the maturation of spirits or other alcoholic beverages, ensuring uniform wood composition and extraction potential throughout the experiment. The identification codes of the brandy samples, together with their alcohol strength before aging and the volume of distillate placed in each barrel, are presented in Table 1.

Each diluted distillate was matured individually for 24 months in its respective barrel under controlled cellar conditions. The maturation cellar was maintained at a stable temperature of 12–15°C, with a relative humidity of 70–80%, minimal light exposure, and adequate ventilation to minimize microbial contamination and evaporative losses. All barrels were stored under identical environmental conditions throughout the maturation period.

Analysis of distillates: basic parameters. Freshly produced Vranec grape distillates, diluted to 40% (v/v) ethanol prior to barrel maturation, were analyzed to determine their basic chemical characteristics using official analytical methods recommended by the International Organization of Vine and Wine (OIV) for spirituous beverages.

The following parameters were determined: alcoholic strength, methanol, higher alcohols, total esters, total aldehydes, total acidity, and dry extract. These analyses were performed according to standardized (OIV 2023) procedures appropriate for each parameter.

All measurements were carried out at the beginning of the experiment to characterize the initial chemical composition and technological quality of the distillates prior to oak barrel maturation.

Establishing these baseline parameters was essential for the correct interpretation of subsequent chemical changes observed during aging. Subsequent analytical monitoring focused specifically on the evolution of furfural during the maturation period.

Determination of furfural. Furfural was quantified by a spectrophotometric method based on derivatization with an aniline - acetate reagent in acidic medium, as described in the analytical literature (Friedemann 1964; Kim et al. 2025) and food analysis guidelines (Food Safety and Standards Authority of India /FSSAI/ 2019).

Prior to analysis, all samples were subjected to simple distillation without rectification. This step was performed to eliminate potential color interferences, since brandy matured in oak barrels develops a yellowish coloration due to the extraction of wood-derived compounds, which may affect spectrophotometric measurements. Simple distillation was preferred over rectification because it allows quantitative recovery of furfural without fractionation, thereby preserving the original composition of volatile aldehydes in the sample. From each 100 mL of brandy, 100 mL of distillate was collected for subsequent analysis.

Table 1. Identification and basic characteristics of Vranec brandy samples before barrel maturation

Sample code	Alcohol strength before aging, %	Volume per barre, L
B1	40.12	225
B2	40.20	225
B3	40.08	225
B4	40.14	225
B5	40.32	225
B6	40.09	225
B7	40.10	225
B8	40.02	225
B9	39.98	225
B10	40.05	225
B11	40.15	225
B12	40.16	225

For the assay, 1 mL of the distillate was transferred into a tightly closed test tube, followed by the addition of 10 mL of freshly prepared aniline acetate reagent. The reagent was prepared by mixing 10 mL of aniline, 100 mL of glacial acetic acid, 20 mL of 5% oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$), and 10 mL of 5% potassium dihydrogen phosphate (KH_2PO_4), and diluting the mixture to 200 mL with 7.5% sodium chloride solution. The reaction mixtures were thoroughly mixed and kept in the dark for 30 minutes to allow complete color development. The reaction is based on the condensation of furfural with aniline to form a Schiff base intermediate, which in an acidic medium further reacts to yield a

stable pink-colored complex. The intensity of the developed color, proportional to furfural concentration, was measured in 10 mm quartz cuvettes at a wavelength of $\lambda_{\text{max}} = 480 \text{ nm}$.

To monitor the kinetics of furfural accumulation during maturation, analyses were performed at time zero (before barrel aging) and after 6, 12, 18, and 24 months of maturation. A calibration curve was constructed using a series of furfural standard solutions prepared from analytical-grade furfural in the concentration range of 0.5-9.0 $\text{mg}\cdot\text{L}^{-1}$. The standards were subjected to the same analytical procedure, except that no prior distillation step was required, since they were prepared in aqueous

solution. The resulting calibration curve was used to calculate furfural concentrations in the brandy samples.

Statistical analysis of furfural changes during.

Maturation. All analytical determinations were performed in triplicate, and results are expressed as mean values $\pm$ standard deviation (SD). Statistical analysis was conducted to evaluate the effect of maturation time on furfural concentration and to assess the variability among samples during oak barrel aging. A one-way analysis of variance (ANOVA) was applied to determine whether maturation time (0, 6, 12, 18, and 24 months) had a statistically significant effect on furfural concentration. When significant differences were detected ($p < 0.05$), Tukey's honestly significant difference (HSD) post-hoc test was used for multiple comparisons between maturation stages. Different superscript letters assigned to mean values indicate statistically significant differences between groups at the 95% confidence level. Pearson correlation analysis was performed to evaluate the relationship between maturation time and furfural concentration. In addition, linear regression analysis was used to describe the overall trend of furfural accumulation during barrel aging and to estimate the coefficient of determination (R^2), which reflects the proportion of variability explained by maturation time. All statistical calculations were carried out using Microsoft Excel (Microsoft Corp., USA). A significance level of $p < 0.05$ was considered for all statistical tests.

Results and Discussion

The chemical composition of the twelve Vranec brandy distillates (B1-B12), determined immediately after dilution to 40% (v/v) ethanol and prior to oak barrel maturation, are presented in Table 2. These parameters define the initial chemical matrix that governs extraction kinetics, chemical reactivity, and sensory evolution during subsequent aging in oak barrels. Ethanol concentration averaged $40.12 \pm 0.09\%$ v/v, with individual values ranging from 39.98 to 40.32% v/v, confirming the precision and reproducibility of the dilution process. This uniformity is technologically important because ethanol serves as the principal solvent during maturation, directly influencing the rate and selectivity of extraction of wood-derived

compounds, including phenolics, lactones, and furanic aldehydes such as furfural (Krüger et al. 2022; Tarko et al. 2023). A consistent alcohol content ensures that changes observed during aging can be primarily attributed to maturation time rather than to differences in solvent strength.

Methanol concentrations averaged $0.18 \pm 0.04\%$ v/v, with values ranging from 0.11 to 0.24% v/v, remaining well below regulatory limits established by the International Organization of Vine and Wine (OIV). These results indicate effective control of fermentation and distillation processes. In grape-derived spirits, methanol formation is associated with enzymatic degradation of pectic substances; therefore, the low levels observed suggest limited pectinolytic activity and appropriate separation of undesirable fractions during distillation. From a toxicological standpoint, methanol represents a critical safety parameter in distilled beverages, and the measured concentrations confirm compliance with international standards (Raičević et al. 2022). Higher alcohols averaged $1417 \pm 165 \text{ mg.L}^{-1}$, with a range of 1110-1623 mg.L^{-1} , values characteristic of young rectified grape distillates. These compounds predominantly propanol, iso-butanol, and isoamyl alcohols originate from yeast amino acid metabolism during fermentation (Hazelwood et al. 2008). While excessive concentrations may contribute to harsh or solvent-like sensory impressions, moderate levels are considered technologically advantageous, as higher alcohols act as precursors for ester formation during maturation (Swiegers et al. 2005). Through esterification reactions with organic acids, these compounds contribute to the gradual development of fruity and floral aromatic nuances, thereby enhancing the complexity of the matured spirit (Krüger et al. 2022).

Total esters averaged $473 \pm 74 \text{ mg.L}^{-1}$, with concentrations ranging from 398 to 623 mg.L^{-1} , while ethyl acetate averaged $237 \pm 37 \text{ mg.L}^{-1}$ (range 198 - 315 mg.L^{-1}). Esters are primary contributors to fresh and fruity aromas, forming the aromatic foundation of the distillate prior to maturation (Sumby et al. 2010).

Ethyl acetate, the predominant ester, enhances aromatic complexity when present at moderate levels but may impart undesirable solvent-like notes at higher concentrations.

Table 2. Chemical parameters of fresh brandy distillates with overall mean and standard deviation

Sample	Ethanol, % v/v	Methanol, % v/v	Higher alcohols, mg.L ⁻¹	Total esters, mg.L ⁻¹	Ethyl acetate, mg.L ⁻¹	Total acids, g.L ⁻¹	Total aldehydes, mg.L ⁻¹	Dry extract, g.L ⁻¹
B1	40.12	0.15	1482.2	519.4	254.4	0.0894	88.5	0.92
B2	40.20	0.18	1380.1	425.7	210.1	0.0851	79.5	1.11
B3	40.08	0.20	1542.5	398.8	201.5	0.0761	69.8	1.85
B4	40.14	0.14	1222.4	622.8	315.6	0.0942	84.5	1.45
B5	40.32	0.11	1520.5	417.7	258.7	0.0880	90.1	1.55
B6	40.09	0.21	1600.5	401.7	221.2	0.0844	74.1	1.25
B7	40.10	0.18	1284.8	522.4	287.4	0.0743	92.5	1.11
B8	40.02	0.23	1623.3	412.5	198.8	0.0825	94.8	0.97
B9	39.98	0.14	1524.8	547.4	222.6	0.0794	96.0	1.14
B10	40.05	0.19	1250.4	400.9	198.7	0.0887	76.9	1.77
B11	40.15	0.24	1110.1	479.6	231.5	0.0698	77.5	1.11
B12	40.16	0.22	1458.8	523.3	241.8	0.0841	87.9	1.41
Mean	40.12	0.18	1417.0	473.0	237.0	0.0830	84.3	1.30
SD	0.090	0.04	165.0	74.25	37.25	0.0070	8.62	0.30

Measured values are expressed as mean $\pm$ SD (standard deviation)

The balanced ratio observed between higher alcohols and esters indicates favorable chemical conditions for the progressive development of a harmonious aromatic profile during barrel aging (Garde-Cerdán & Ancín-Azpilicueta, 2006).

Total acidity averaged 0.083 ± 0.007 g.L⁻¹, with a range of 0.070–0.094 g.L⁻¹, reflecting the removal of nonvolatile organic acids during distillation. This reduced acidity contributes to a smoother mouthfeel and decreased perception of sharpness in young distillates. During maturation, slow oxidative reactions and interactions with wood-derived components may further modify acidity, contributing to structural balance. Total aldehydes averaged 84.34 ± 8.62 mg.L⁻¹, with individual values ranging from 69.8 to 96.0 mg.L⁻¹. These compounds, predominantly acetaldehyde, are characteristic of fresh distillates and may initially impart pungent or sharp sensory attributes (Wo 2025). However, aldehydes are highly reactive and participate in multiple reactions during maturation, including acetal formation with ethanol and condensation with phenolic compounds extracted from oak. Such transformations generally reduce sensory harshness and promote integration within the overall aromatic matrix of matured brandy (Tarko et al. 2023; Guerrero-Chanivet et al. 2022).

Dry extract values averaged 1.30 ± 0.30 g.L⁻¹, with a range of 0.92–1.85 g.L⁻¹, reflecting trace amounts of non-volatile congeners. Although low at this stage, dry extract content is expected to increase during barrel aging as a result of extraction of wood-derived substances, contributing to body and mouthfeel (Canas 2017). Collectively, these physicochemical parameters indicate that the fresh Vranec brandy distillates exhibit a balanced and technologically appropriate composition. The presence of moderate levels of aroma precursors and low acidity, provides a favorable matrix for controlled extraction of wood-derived constituents and progressive chemical transformations during maturation. Consequently, subsequent sensory and chemical changes observed during aging can be interpreted primarily as a result of barrel-induced processes rather than variations in the initial distillate composition.

Furfural dynamics during barrel maturation

Furfural is a key furanic aldehyde in oak-aged brandy, contributing to aroma complexity while also serving as an indicator of wood influence during maturation. In fresh distillates, furfural originates primarily from the heat-induced degradation of sugars during distillation.

During barrel aging, however, its concentration becomes increasingly governed by extraction from toasted oak, where thermal degradation of hemicelluloses generates furanic compounds that gradually migrate into the brandy.

Monitoring furfural therefore provides insight into both technological processing and the chemical

evolution of brandy during storage. The concentrations of furfural measured in the twelve brandy samples (B1–B12) at 0, 6, 12, 18, and 24 months of maturation are presented in Table 3. Fresh distillates already contained measurable concentrations of furfural (0.56 - 1.12 mg.L⁻¹), confirming partial formation during distillation.

Table 3. Evolution of furfural concentration (mg.L⁻¹) in brandy samples during barrel maturation

Sample	0 months (fresh distillates)	6 months	12 months	18 months	24 months
B1	0.56	1.14	2.20	5.66	5.66
B2	0.66	2.22	3.07	5.24	5.22
B3	1.12	1.09	2.12	3.44	3.43
B4	0.98	1.12	2.15	4.85	4.85
B5	1.10	2.01	3.01	5.14	5.13
B6	0.88	2.09	2.95	3.89	3.89
B7	0.76	2.11	3.22	6.89	6.89
B8	0.59	1.13	2.56	4.22	4.21
B9	0.61	1.22	2.26	5.05	5.06
B10	0.82	2.13	3.00	5.51	5.50
B11	0.65	1.15	2.19	4.65	4.65
B12	0.74	1.10	3.01	5.54	5.55

After 6 months of barrel aging, furfural concentrations increased to 1.09 - 2.22 mg.L⁻¹, indicating the onset of extraction of wood-derived furanic aldehydes. A continued rise was observed at 12 months (2.12 - 3.22 mg.L⁻¹), demonstrating progressive release of thermally degraded hemicellulose products from the oak matrix. The most pronounced increase occurred between 12 and 18 months, when furfural concentrations rose sharply to 3.44 - 6.89 mg.L⁻¹. This stage reflects intensified extraction, facilitated by ethanol acting as an efficient solvent for furanic compounds and enhanced diffusion from the toasted wood structure. After 18 months, furfural concentrations showed little further change and remained within a similar range at 24 months, indicating that the system approached a dynamic equilibrium between continued extraction and chemical transformation or loss of furfural within the brandy. To better describe the overall maturation trend, the mean furfural concentrations with standard deviation are summarized in Table 4. The average value increased from 0.79 mg.L⁻¹ at time zero to 1.55 mg.L⁻¹ at 6 months, 2.65 mg.L⁻¹ at 12 months, and 5.01 mg.L⁻¹

at 18 months, with only a minimal change thereafter (5.01 mg.L⁻¹) at 24 months. The larger standard deviation observed at 18 and 24 months indicates greater variability among barrels as wood–brandy interactions progressed. The superscript letters shown in Table 4 represent the results of Tukey's HSD post-hoc test. Different letters indicate statistically significant differences between maturation times ($p < 0.05$). The grouping shows that each stage up to 18 months differs significantly from the previous one, whereas the 18- and 24-month samples belong to the same statistical group, confirming stabilization.

Statistical evaluation further confirmed that maturation time had a highly significant effect on furfural concentration. One-way ANOVA results are presented in Table 5. The calculated F value ($F = 106.75$) was far higher than the critical F value ($F_{crit} = 2.54$) at $\alpha = 0.05$, while the probability value was extremely low ($p = 3.02 \times 10^{-25}$). These results demonstrate that the observed increase in furfural is not due to random variation but represents a systematic time-dependent process.

Table 4. Mean furfural concentration (mg.L⁻¹) in Vranec brandy during oak barrel maturation, expressed as mean $\pm$ standard deviation (n = 12). Different letters indicate statistically significant differences among maturation times according to Tukey's HSD test (p < 0.05)

Maturation time, months	Furfural, Mean $\pm$ SD, mg.L ⁻¹	Tukey group
0	0.79 $\pm$ 0.19	a
6	1.54 $\pm$ 0.51	b
12	2.65 $\pm$ 0.43	c
18	5.01 $\pm$ 0.91	d
24	5.01 $\pm$ 0.91	d

Values are means of 12 brandy samples analyzed at each maturation time. Different superscript letters (a–d) denote statistically significant differences between time points.

Table 5. Results of one-way ANOVA evaluating the effect of maturation time on furfural concentration in Vranec grape brandy

Source of variation	SS	df	MS	F	p-value	F crit
Between groups	182.14	4	45.53	106.75	3.02 x 10 ⁻²⁵	2.54
Within groups	23.46	55	0.43			
Total	205.60	59				

SS – sum of squares; df – degrees of freedom; MS – mean square; F – F statistic; p-value – probability level; 0 F crit – critical F value at $\alpha = 0.05$

The evolution of mean furfural concentration as a function of maturation time is illustrated in Figure 1. The curve shows a gradual increase during the first year, followed by a steep rise between 12 and 18 months and subsequent stabilization. The fitted regression model ($R^2 = 0.93$) confirms a strong time dependence, while the deviation from linearity at the final stage reflects the plateau phase.

Several mechanisms explain the stabilization observed after 18 months. First, the availability of extractable furfural precursors in oak wood decreases over time, as most hemicellulose-derived compounds are released during the initial stages of aging (Puech 1984).

Second, once in the distillate, furfural undergoes secondary reactions such as oxidation to furanic acids, condensation with amino compounds, or polymerization with phenolic substances, which reduce its free measurable concentration. Third, the barrel itself acts as a regulating system, with part of the furfural being reabsorbed into the wood

structure or lost through volatilization during storage, a phenomenon known as the “angel’s share” (Singleton 1995).

From a sensory perspective, furfural is associated with caramel, toasted, almond-like, and baked-bread notes typical of matured brandy. Stabilization of furfural concentration after 18 months prevents excessive dominance of wood-derived aromas and helps preserve balance with fruity esters. From a toxicological perspective, the measured concentrations remain far below levels of concern and therefore represent a maturation marker rather than a safety issue. Overall, furfural exhibits a clear time-dependent accumulation during barrel aging of brandy, with the most rapid increase occurring between 12 and 18 months, followed by stabilization.

This behavior confirms its dual origin from both distillation and oak wood and highlights its usefulness as an indicator of maturation progress and wood influence in brandy.

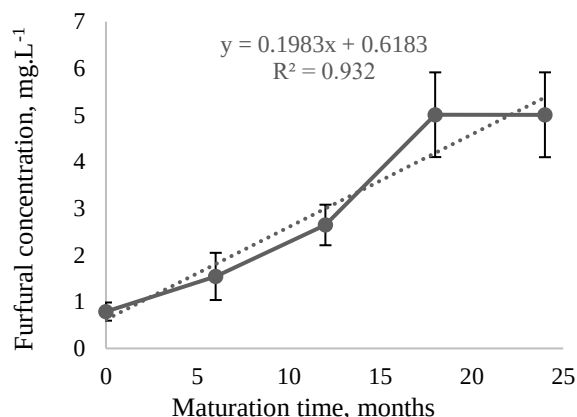


Figure 1. Evolution of furfural concentration in Vranec grape brandy during 24 months of maturation in medium-toast Hungarian oak barrels (mean $\pm$ SD, $n = 12$). The dashed line represents the linear regression model ($R^2 = 0.932$)

Conclusions

The present study suggests that furfural may serve as a useful chemical marker of oak barrel maturation in industrially produced Vranec grape brandy under the experimental conditions investigated. Detectable concentrations were already present in fresh distillates due to thermal sugar degradation during distillation, whereas the dominant contribution to furfural accumulation originated from oak wood during aging.

A clear time-dependent increase in furfural concentration was observed throughout the 24-month maturation period. The most pronounced rise occurred between 12 and 18 months, corresponding to intensified extraction of hemicellulose-derived compounds from toasted oak. After 18 months, furfural levels stabilized, indicating that the system reached a dynamic equilibrium between continued extraction and concurrent chemical transformation or loss processes within the brandy. Statistical analysis demonstrated that maturation time had a highly significant effect on furfural concentration, while post-hoc comparisons showed that the stabilization phase between 18 and 24 months was not statistically different.

The observed furfural concentrations contributed positively to the sensory profile of the matured brandy by enhancing caramel, toasted, and bakery-like aromatic notes characteristic of oak-aged

spirits. At the same time, furfural levels remained well below toxicological thresholds, indicating that its presence may be considered a quality indicator rather than a safety concern under the technological conditions applied in this study.

Overall, the results indicate that controlled oak barrel maturation plays an important role in the chemical evolution of industrially produced brandy. Monitoring furfural may provide useful information on maturation progress, wood influence, and the optimization of aging duration, thereby supporting quality improvement and process standardization in industrial brandy production.

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Author Contributions

Conceptualization, A.P. and V.D.; methodology, A.P. and V.D.; formal analysis, A.P.; investigation, A.P.; resources, A.P. and V.D.; data curation, A.P.; writing - original draft preparation, A.P.; writing - review and editing, A.P. and V.D.; visualization, A.P.; supervision, V.D. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflicts of interest.

References

- Arduini S., Chinnici F. Influence of oak wood seasoning duration and toasting degree on endogenous and wood-derived compounds of Brandy Italiano. *Food and Bioprocess Technology*, 2026, 19(12): 38. <https://doi.org/10.1007/s11947-025-04115-x>
- Batista F.R.M., Meirelles A.J.A. Computer simulation applied to studying continuous spirit distillation and product quality control. *Food Control*, 2011, 22(10): 1592-1603. <https://doi.org/10.1016/j.foodcont.2011.03.015>
- Canas S. Phenolic composition and related properties of aged wine spirits: Influence of barrel characteristics. *Beverages*, 2017, 3(4): 55. <https://doi.org/10.3390/beverages3040055>
- Capuano E., Fogliano V. Acrylamide and 5-hydroxymethylfurfural (HMF): A review on metabolism, toxicity, occurrence in food and mitigation strategies. *LWT. Food Science and Technology*, 2011, 44(4): 793-810. <https://doi.org/10.1016/j.lwt.2010.11.002>
- Chatonnet P., Dubourdieu D. Comparative study of the characteristics of American white oak (*Quercus alba*) and European oak (*Quercus petraea* and *Q. robur*) for production of barrels used in barrel aging of wines. *American Journal of Enology and Viticulture*, 1998, 49(1): 79-85. <https://doi.org/10.5344/ajev.1998.49.1.79>
- Claus M.J., Berglund K.A. Fruit brandy production by batch column distillation with reflux. *Journal of Food Process Engineering*, 2005, 28(1): 53-67. <https://doi.org/10.1111/j.1745-4530.2005.00377.x>
- Conner J.M., Paterson A., Piggott J.R. Changes in wood extractives from oak cask staves through maturation of Scotch malt whisky. *Journal of the Science of Food and Agriculture*, 1993, 62(2): 169-174. <https://doi.org/10.1002/jsfa.2740620210>
- du Plessis H.W., Steger C.L.C., Du Toit M., Lambrechts M. The occurrence of malolactic fermentation in brandy base wine and its influence on brandy quality. *Journal of Applied Microbiology*, 2002, 92(5): 1005-1013. <https://doi.org/10.1046/j.1365-2672.2002.01616.x>
- Scientific Panel on Methods of Sampling and Analysis of FSSAI. *Manual of Methods of Analysis of Foods: Alcoholic Beverages. 2.0 Determination of Ethyl alcohol content* (Third Edition) Food Safety and Standards Authority of India. Ministry of Health and Family Welfare, Government of India. 2019, 64 pages. Available at: https://fssai.gov.in/upload/uploadfiles/files/Manual_Alcoholic_Beverages_04_07_2019.pdf
- Friedemann T.E., Keegan P.K., Witt N.F. Determination of furan aldehydes: Reaction with aniline in acetic and hydrochloric acid solutions. *Analytical Biochemistry*, 1964, 8(3): 300-311. [https://doi.org/10.1016/0003-2697\(64\)90061-2](https://doi.org/10.1016/0003-2697(64)90061-2)
- Garde-Cerdán T., Rodríguez-Mozaz S., Ancín-Azpilicueta C. Volatile composition of aged wine in used barrels of French oak and of American oak. *Food Research International*, 2002, 35(7): 603-610. [https://doi.org/10.1016/S0963-9969\(01\)00151-X](https://doi.org/10.1016/S0963-9969(01)00151-X)
- Garde-Cerdán T., Ancín-Azpilicueta C. Effect of oak barrel type on the volatile composition of wine: Storage time optimization. *Food Science and Technology*, 2006, 39(3): 199-205. <https://doi.org/10.1016/j.lwt.2005.01.009>
- Guerrero-Chanivet M., Valcárcel-Muñoz M.J., Guillén-Sánchez D.A., Castro-Mejías R., Durán-Guerrero E., Rodríguez-Dodero C., García-Moreno M. de V. Influence of sulfur dioxide, the distillation system and the aging conditions on the final sensory characteristics of brandy. *Foods*, 2022, 11(21): 3540. <https://doi.org/10.3390/foods11213540>
- Hazelwood L.A., Daran J.M., van Maris A.J.A., Pronk J.T., Dickinson J.R. The Ehrlich pathway for fusel alcohol production: A century of research. *Applied and Environmental Microbiology*, 2008, 74(8): 2259-2266. <https://doi.org/10.1128/AEM.02625-07>
- Joint FAO/WHO Expert Committee on Food Additives (JECFA). Safety evaluation of certain food additives and contaminants: Furfural. In: *WHO Food Additives Series* (Vol. 46). World Health Organization, Geneva, 2001, 206 pages, Print ISBN: 92-5-104508-9. Available at: https://www.inchem.org/documents/jecfa/jecmono/v46j_e01.htm
- Kim E., Jun T., Kim A.R., Kwak B.S., Park H. Selective green colorimetric liquid- and solid-based determination of furfural in power transformer insulating fluid. *ACS Omega*, 2025, 10(33): 37025-37038. <https://doi.org/10.1021/acsomega.5c00572>
- Krüger R.T., Alberti A., Nogueira A. Current technologies to accelerate the aging process of alcoholic beverages: A review. *Beverages*, 2022, 8(4): 65. <https://doi.org/10.3390/beverages8040065>
- Léauté R. Distillation in lambic: A historical and technical review. *American Journal of Enology and Viticulture*, 1990, 41(1): 90-103. <https://doi.org/10.5344/ajev.1990.41.1.90>
- Lee K.-Y.M., Paterson A., Piggott J.R., Richardson G.D. Origins of flavour in whiskies and a revised flavour wheel: A review. *Journal of the Institute of Brewing*, 2001, 107(5): 287-313. <https://doi.org/10.1002/j.2050-0416.2001.tb00099.x>
- Morales F.J. Hydroxymethylfurfural (HMF) and Related Compounds. In: *Process-Induced Food Toxicants: Occurrence, Formation, Mitigation, and Health Risks*, (R.H. Stadler, D.R. Lineback Eds.). John Wiley & Sons, Inc. 2009, pp. 135-174, Print ISBN:

- 9780470074756, eBook ISBN: 9780470430101, <https://doi.org/10.1002/9780470430101.ch2e>
- Mosedale J.R. Effects of oak wood on the maturation of alcoholic beverages with particular reference to whisky. *Forestry: An International Journal of Forest Research*, 1995, 68(3): 203-230. <https://doi.org/10.1093/forestry/68.3.203>
- Mosedale J.R., Puech J.L. Wood maturation of distilled beverages. *Trends in Food Science & Technology*, 1998, 9(3): 95-101. [https://doi.org/10.1016/S0924-2244\(98\)00024-7](https://doi.org/10.1016/S0924-2244(98)00024-7)
- Sub-commission of methods of analyses. Enology Commission of OIV (International Organisation of Vine and Wine). *Compendium of International Methods of Analysis of Spirituous Beverages of Vitivinicultural origin*. OIV: Dijon, France. 2023, 290 pages. <https://www.oiv.int/what-we-do/standards>
- Patil K. Distillation Operations: Methods, Operational and Design Issues (Version 2). ChemRxiv. 2023, 9 pages. <https://doi.org/10.26434/chemrxiv-2022-g36d7-v2>
- Puech J.L. Characteristics of oak wood and biochemical aspects of Armagnac Aging. *American Journal of Enology and Viticulture*, 1984, 35(1): 77-81. <https://doi.org/10.5344/ajev.1984.35.2.77>
- Raičević D., Popović T., Jančić D., Šuković D., Pajović-Šćepanović R. The impact of type of brandy on the volatile aroma compounds and sensory properties of grape brandy in Montenegro. *Molecules*, 2022, 27(9): 2974. <https://doi.org/10.3390/molecules27092974>
- Ribèreau-Gayon P., Dubourdieu D., Donèche B., Lonvaud A. *Handbook of Enology: Volume 1. The Microbiology of Wine and Vinifications* (2nd ed.). Chichester: John Wiley & Sons. 2006, 512 pages. Print ISBN: 978-0-470-01034-1; e-Book ISBN: 978-0-470-01035-8, O-Book ISBN /Online Library/: 978-0-470-01036-5, <https://doi.org/10.1002/0470010363>
- Singleton V.L. Oxygen and wine aging: Beyond the bubbles. *American Journal of Enology and Viticulture*, 1995, 46(2): 196-203. <https://doi.org/10.5344/ajev.1995.46.2.196>
- Śliwińska M., Wiśniewska P., Dymerski T., Wardencki W., Namieśnik J. The flavour of fruit spirits and fruit liqueurs: A review. *Flavour and Fragrance Journal*, 2015, 30(3): 197-207. <https://doi.org/10.1002/ffj.3237>
- Sumby K.M., Grbin P.R., Jiranek V. Microbial modulation of aromatic esters in wine. *Food Chemistry*, 2010, 121(1): 1-16. <https://doi.org/10.1016/j.foodchem.2009.12.004>
- Swiegers J.H., Bartowsky E.J., Henschke P.A., Pretorius I.S. Yeast and bacterial modulation of wine aroma and flavour. *Australian Journal of Grape and Wine Research*, 2005, 11(2): 139-173. <https://doi.org/10.1111/j.1755-0238.2005.tb00285.x>
- Syguła E., Łyczko J., Koziel J.A., Białowiec A. Furfural release from lignocellulosic biomass biochars: Environmental and health implications. *Industrial Crops and Products*, 2025, 237(): 122855. <https://doi.org/10.1016/j.indcrop.2025.122855>
- Tarko T., Krąkowski F., Duda-Chodak A. The impact of compounds extracted from wood on the quality of alcoholic beverages. *Molecules*, 2023, 28(2): 620. <https://doi.org/10.3390/molecules28020620>
- Wang L., Chen S., Xu Y. Distilled beverage aging: A review on aroma characteristics, maturation mechanisms, and artificial aging techniques. *Comprehensive Reviews in Food Science and Food Safety*, 2022, 22(1): 502-534. <https://doi.org/10.1111/1541-4337.13080>
- Wo X. A comparative study of the important aroma components of brandy and rum. *International Journal of Agriculture and Food Sciences Research*, 2025, 3(1): 8-20. <https://doi.org/10.62051/ijafsr.v3n1.02>
- Yagishita M., Reber O., Alter D., Kölling R., Einfalt D. Effect of partial condensation (dephlegmation) in fruit brandy distillation equipment on the composition of apple brandies. *Beverages*, 2025, 11(2): 52. <https://doi.org/10.3390/beverages11020052>
- Yoncheva T., Stoyanov N., Dimitrov D. Influence of oak wood on the chemical and organoleptic profile of white wines. *Food Science and Applied Biotechnology*, 2024, 7(1): 79-91. <https://doi.org/10.30721/fsab2024.v7.i1.315>