

Article

Characterisation of Cork Volatile Organic Compounds Using TD-GC-MS: Effects of Origin, Washing Process, and Thermal Processing of Cork Stoppers

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Abstract: This study presents a green and solvent-free methodology based on thermal desorption coupled to gas chromatography-mass spectrometry (TD-GC-MS) to characterise cork's volatile aromatic (VOC) profile. Samples from three geographical origins—Catalonia, Extremadura, and Sardinia—were analysed at different extraction temperatures. Cork stoppers from Sardinia were also analysed after two washing procedures (immersion and spray) and thermal treatment. The results showed that temperature and geographical origin significantly influenced the quantity and intensity of extracted VOCs, with higher extraction temperatures yielding a more comprehensive volatile profile. Vanillin was the most abundant compound in all samples. A multivariate analysis showed that cork from Extremadura was associated with carboxylic acids, Catalonia with furan derivatives and sugar-related compounds, and Sardinia with phenolic compounds linked to lignin degradation. Immersion-washed stoppers retained more lignin-derived and phenolic compounds, while spray-washed samples were characterised by a higher alkane content. Thermal treatment notably altered the VOC profile, increasing ketones such as acetophenone and 2-nonadecanone and reducing alkanes and fatty acids. These findings highlight the influence of the geographical origin and manufacturing process on the aromatic composition of cork, with potential applications in industries seeking natural active compounds.



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Keywords: *Quercus suber* L.; cork; volatile organic compounds; TD-GC-MS

1. Introduction

Quercus suber L., or cork oak, has ecological and social values. Cork oak landscapes exemplify a well-balanced relationship between sustainable management and forest conservation. This forest plays a significant role in carbon retention, regulates the hydrological cycle, helps prevent the advancement of soil desertification, and constitutes a unique ecosystem with important biodiversity [1]. Furthermore, the cork oak forest supports hundreds of companies and employs thousands of people as it is the origin of highly valuable products such as cork stoppers.

Due to their physical properties, such as high flexibility, elasticity, compressibility, or impermeability to liquid, cork stoppers are a perfect closure for sealing still and sparkling wines [2]. Cork is used in various other applications, including construction, automotive, and textiles [3]. The cork stopper is the main product of the cork industry, and its by-products are the raw material for other auxiliary or satellite industries. Utilising cork

by-products to develop new cork products leads to improving the future of cork oak forests, preventing land abandonment, and promoting the use of products based on biomass.

The combination of cork properties depends on factors such as its chemical composition and/or cellular structure [4]. Cork of *Quercus suber* L. comprises suberin, lignin, polysaccharides, extractives, and other minor components [4,5]. Extractives comprise a heterogeneous group of molecules, mainly aliphatic, triterpene, and phenolic compounds [6–8], that can be extracted from cork stoppers using a hydroalcoholic solution.

Cork also contains many volatile organic compounds (VOCs), including alcohols, fatty acids, ethyl esters, and acetic acid esters [9–17]. Some of them are associated with the presence of specific microflora on the tree and cork slabs [13,14,18] and others are the result of reactions related to the restructuration of some macromolecular compounds such as lignin [7,13,17] and possibly also suberin [7,15]. The volatile compounds extracted from cork seem to differ according to the stage of the production process: cork bark presents a different aromatic profile than cork stoppers [2], and other industrial cork by-products also show different aromatic fractions [8]. Likewise, the porosity level in natural cork stoppers can influence volatile organic compound (VOC) extraction [9], and granulated cork shows higher amounts of VOCs than cork stoppers [18].

Evidence shows that some of cork's extractives or VOCs can positively contribute to wine's aroma, colour, or astringency [8–20]. Some are associated with health benefits related to their antioxidative activities [10,19,21], among other benefits.

Aromatic compounds can be used as flavours or fragrances in various consumer goods such as food and beverages, pharmaceuticals, and/or cosmetic products. The aroma industry experienced a predicted compound annual growth rate (CAGR) of 6.2% between 2016 and 2024. The number of consumers who prefer natural products over synthetic ones is increasing, and developing green and sustainable methodologies to obtain aromas is considered to be a demand in this sector [22]. The estimated worldwide demand for natural aromatic compounds in cosmetic products as a flavouring was approximately USD 21.8 billion in 2011 [23], which is expected to increase. Natural aromas are directly extracted from natural sources, and others are produced through the biotransformation of substrates isolated from plants using physical extraction, enzymatic, or microbial processes [24].

The development of green and sustainable procedures to extract VOCs has been considered to be a substantial challenge launched by the competitiveness of some industries and environmental protection [25]. In general, extraction steps take several hours or longer. They are frequently carried out by prolonged macerating and/or stirring in a solvent, followed by prolonged procedures to eliminate the solvent [26]. In the case of cork, many methodologies to extract aromas from cork use solvents [7,8,12,19,20]. In this context, developing solvent-free techniques is of great interest to make conventional processes greener, cleaner, safer, and easier to perform [27,28].

In this work, a green, solvent-free extraction technique was employed to obtain the volatile profile of cork from *Quercus suber* L. Thermal desorption coupled to gas chromatography-mass spectrometry (TD-GC-MS) was used for the extraction, identification, and relative quantification of VOCs from cork without any previous solvent extraction. A range of extraction temperatures was used to evaluate their effect on the number and abundance of extracted VOCs. Cork from three geographical locations—Extremadura, Catalonia, and Sardinia—were analysed. The impact of a two-step cork stopper manufacturing process on the VOC profile was also evaluated. For this reason, cork barks from Sardinia were used to manufacture cork stoppers that were submitted to two washing processes (aspersion or immersion), with or without thermal treatment. Normalisation, a principal component analysis (PCA), and a head map with clustering were used to interpret

the statistical biological volatile profile. This knowledge benefits not only the cork and wine industry in understanding the aromatic evolution of its products but also sectors such as food, cosmetics, or pharmaceuticals, which seek valuable compounds to enhance their products.

2. Materials and Methods

2.1. Sample Preparation

Six types of cork sample were studied (Table 1). The effect of geographical origin was evaluated by analysing the cork barks of *Quercus suber* L. (without boiling) from the following three geographical regions: Catalonia (CAT) (North of Spain), Extremadura (EXT) (south of Spain), and Sardinia (SAR) (Italy). Six cork slabs (150 cm × 20 cm × 5 cm) of each sample were supplied by JVIGAS, S.A. (Palafrugell, Spain). Then, three random cork slabs from Sardinia were selected to produce cork stoppers following the traditional manufacturing process. After punching out cork stoppers, a portion was washed using an immersion procedure (BA) and the other half was washed using a spray procedure (RA). The BA procedure submerged the stoppers in hot water at approximately 75 °C for 60 min with no chemical additives. In the RA procedure, cork stoppers were exposed to hot water sprayed at approximately 60 °C for 20 min without using solvents or chemical agents. These procedures followed the company's internal protocols and were applied without modification to reflect real industrial conditions. Half of the cork stoppers were washed using the RA procedure and treated at 100 °C for 24 h (TT). All samples (cork barks and natural cork stoppers) were cut into small pieces (<10 mm), ground with a ZM-200 ultra centrifugal mill (Retsch, The Netherlands), and filtered with a sieve shaker (Cisa, Spain) to obtain granulometric fractions of 40 to 60 mesh (0.25 to 0.42 mm grain size) that were used for the subsequent analyses.

Table 1. Geographical origin, coordinates, type of samples, manufacturing processes implemented, and code of the analysed samples.

Geographical Origin	Coordinates (Decimal Degrees)	Type of Sample	Manufacturing Processes Implemented	Code
Catalonia	41.883° N, 2.975° E	Raw cork	None	CAT
Extremadura	38.1127° N, −6.49561° W	Raw cork	None	EXT
Sardinia	39.169° N, 8.654° E	Raw cork	None	SAR
		Cork stoppers	Washing by immersion	BA
			Washing by a spray without thermal treatment	RA
			Washing by a spray with thermal treatment	TT

2.2. Thermal Desorption Extraction (TD)

The thermal desorption methodology was carried out in two stages, as listed in Jové et al., 2021 [29]. In total, 0.5 g of each sample was placed in an empty stainless steel thermal desorption tube (6 mm O.D. × 90 mm long, 5 mm I.D.; Markes International Limited, Pontyclun, UK) and introduced into a desorption unit (DU). Then, each tub was heated inside the DU at different extraction temperatures (from 80 °C to 220 °C) for 10 min using helium as the carrier gas at a flow rate of 40 mL min^{−1} and with an inlet split of 20 mL min^{−1}. The extracted compounds were focused on a cold trap at −20 °C packed with Tenax TA (90 mg and 20–35 mesh; Chrompack, Middelburg, The Netherlands) after being

previously preconditioned at 300 °C for eight hours. Then, the concentrated compounds were sent to the GC column by rapidly heating the trap at 330 °C with a 20 mL min^{−1} outlet split. After injection, the trap was cleaned by setting the hold time to 10 min at 330 °C. Extraction compounds were identified at different selected temperatures from 80 to 220 °C.

2.3. Gas Chromatography-Mass Spectrometry (GC-MS) Analysis of the Thermally Desorbed Compounds

GC-MS was performed using an Agilent 6890N chromatograph equipped with a Gerstel MPS2 autosampler coupled to an Agilent 5973N mass spectrometer. The separation was achieved using an HP-5MS column (30 m, 0.25 mm, and 0.25 µm film thickness) (J&W Scientific, Folsom, CA, USA) and a GC oven programme starting at 50 °C (3 min), increasing by 6 °C min^{−1} to 325 °C (held for 20 min). The carrier gas was helium (99.999%) from Abello Linde (Barcelona, Spain), with a constant flow rate of 1 mL min^{−1}. The transfer line temperature was set at 300 °C and the ion source temperature was set at 250 °C. All mass spectra were acquired at an electron impact energy of 70 eV. The mass range was 35–600 *m/z*, with a scan rate of 6 scans s^{−1}. The analysis was performed in full-scan mode. All the samples were analysed in triplicate. Cork volatiles were identified based on the mass spectra of the National Institute of Standards and Technology (NIST) MS spectral library using a minimum match-quality criterion of 75%. The relative percentages of detected peaks were obtained by normalising the peak areas, with all relative response factors being set to one.

2.4. Statistical Data Analyses

A general linear model was employed to evaluate the effect of temperature (T) and geographical origin (GO). Then, to visualise the overall distribution of VOCs across geographic origins, presence-absence data were generated and Venn diagrams and UpSet plots were created. A principal component analysis (PCA) was also performed.

The study of the effect of the washing type and thermal treatment analysed the results using multivariate techniques, including a principal component analysis (PCA), heat map, and hierarchical clustering. All statistical data analyses were performed using R Statistical Software (version 4.3.2).

3. Results

3.1. TD-GC-MS as a Methodology to Obtain the Volatile Aromatic Profile of Cork

The first step in studying cork volatile profile characteristics is to obtain as many complete volatile components as possible. For this reason, cork samples from different geographical origins—Catalonia (CAT), Extremadura (EXT), and Sardinia (SAR)—were subjected to an increase in temperature from 80 to 220 °C, with an analysis of the extracts obtained for each temperature step. The maximum temperature of 220 °C was selected based on preliminary trials as it allowed an efficient release of VOCs while avoiding thermal degradation or the formation of artefacts that could distort the native volatile profile of the cork.

Figure 1 shows the sum of the peak areas of all extracted compounds derived from each temperature point and geographical origin as well as the number of extracted compounds.

The sum peak area and the number of extracted compounds increased as the temperature increased. Generally, higher temperatures and longer times facilitate vaporisation and, therefore, the extraction of VOCs from cork samples [30]. A general linear model was employed to evaluate the effect of temperature (T) and sample geographical origin (GO) on the number of compounds extracted from the cork. The temperature factor was assessed at six levels (100, 140, 160, 180, 200, and 220 °C), while the geographical origin

factor comprised three levels (CAT, EXT, and SAR). The analysis of variance revealed statistically significant effects for both temperature and origin. The regression analysis confirmed that temperature significantly impacted the area, with higher values observed as the temperature increased. The coefficient for temperature (T) was positive and highly significant ($p < 0.000$), indicating that a unit increase in temperature led to a substantial increase in area. Regarding the sample origin, the results showed that samples from EXT had significantly larger areas than CAT ($p = 0.004$). In contrast, samples from SAR did not show a statistically significant difference from CAT ($p = 0.173$). These findings suggested that temperature and sample origin influenced the VOC area, with the greatest extraction occurring at higher temperatures, particularly in samples from EXT. However, the non-significant difference between SAR and CAT indicated that their effect on the area might be similar. The model's R^2 value of 82.43% showed that the predictors (temperature and geographical origin of the cork) accounted for a substantial portion of the variability in the number of VOCs. Following this, the samples were submitted to all temperature ranges to obtain the complete volatile profile of the cork.

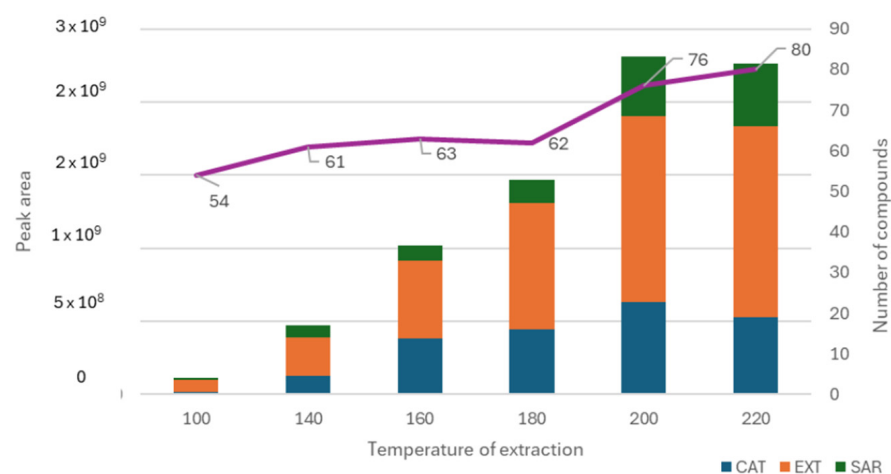


Figure 1. The sum of the peak area of extracted compounds obtained at different extraction temperatures from different geographical origins. It also shows the number of extracted compounds at different temperatures.

3.2. Volatile Aromatic Profile of Cork with Different Geographical Origins

Typical volatile profile chromatograms of cork obtained by TD-GC-MS are illustrated in Figure 2.

The aromatic profiles of the cork samples susceptible to being extracted by thermal desorption at all selected temperatures are represented in Table S1 in Supplement Materials. Consequently, 104 compounds extracted from the analysed samples were identified, including 70 in CAT, 94 in SAR, and 50 in EXT. Most of these VOCs have been described previously [8,9,11,13,18–20,31–42] but some have not because the extractives of cork vary depending on the methodology used [43] and the type of sample [8,9,19]. According to the different functional groups, these cork volatiles could be classified into eleven groups, including aldehydes (10), alkanes (19), aromatic compounds (7), carboxylic acids (8), esters (4), fatty acids (7), fatty alcohols (5), furans (7), ketones (8), and phenolic compounds (10). Finally, eighteen compounds were classified under the “Others” category, exhibiting structures characteristic of heterocyclic nitrogen compounds, carbohydrates (sugars), or heterocyclic hydroxypyridines.

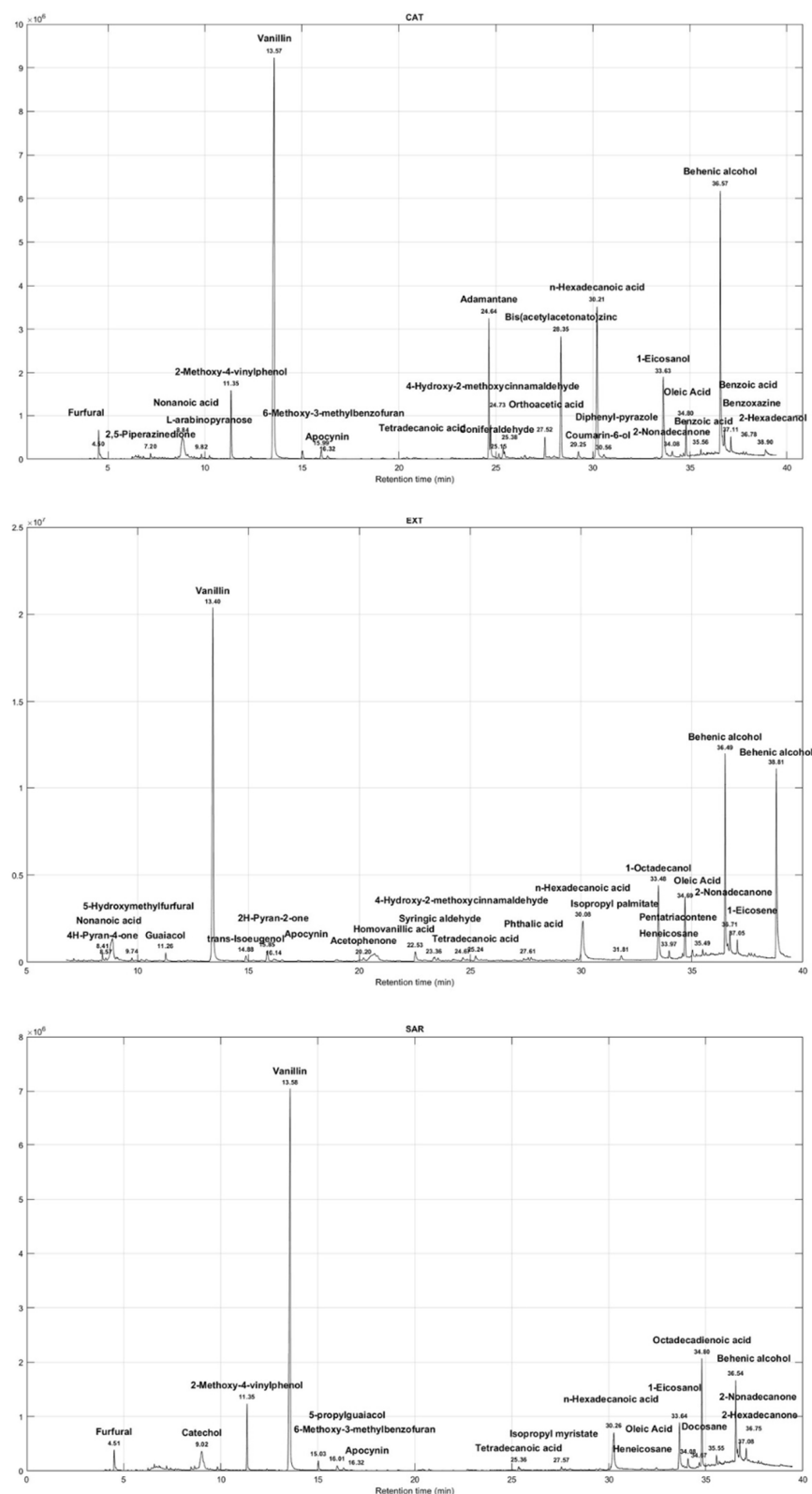


Figure 2. Mass spectra of cork from Catalonia (CAT), Extremadura (EXT), and Sardinia (SAR) were obtained by gas chromatography-mass spectrometry (GC-MS) using the SCAN model.

The percentage composition, calculated based on the total area of each compound in the sample, provided insights into their relative representation across different regions. Several compounds exhibited notable differences in their distribution. For instance, vanillin was the most abundant compound across all origins, with 33.58% in CAT, 31.36% in EXT,

and 41.51% in SAR, indicating a common presence but varying abundances. Additionally, cycloeicosane (11.55%) was highly prevalent in CAT, lower in SAR (0.2%), and absent in EXT, whereas behenic alcohol showed the highest concentration in EXT (14.40%) compared with 6.34% in CAT and 4.62% in SAR. Furthermore, some compounds exhibited regional differences, such as n-hexadecanoic acid, which was most abundant in EXT (7.01%), and 2-methoxy-4-vinylphenol, which was highly concentrated in SAR (8.62%) and CAT (7.87%) while remaining significantly lower in EXT (1.20%).

Vanillin has a significant impact on the overall aromatic profile of cork. Its derivatives are the most widely used aromatic compounds in food and cosmetics. Hence, there is an increasing demand for its natural sources [44]. Natural and synthetic vanillin have been used as flavouring agents due to their pleasant aroma, which features sweet and floral notes. 2-Methoxy-4-vinylphenol is used as a fragrance and is anti-inflammatory [45]. Due to its antioxidant and flavour activities, n-hexadecanoic acid has been utilised as a functional ingredient in the cosmetic industry.

To assess the distribution of all identified VOCs across three geographical origins, a Venn diagram and an UpSet plot were used (Figure 3). Thirty-nine compounds were common to all three regions: twenty-six VOCs were unique to SAR, while twenty-five were shared exclusively between CAT and SAR. EXT shared fewer exclusive compounds with the other areas, suggesting a greater chemical overlap with CAT than with SAR. To highlight the most abundant VOCs, we annotated the Venn diagram for compounds with a relative area greater than 5%. These included vanillin, cycloeicosane, 2-methoxy-4-vinylphenol, and behenic alcohol in CAT; vanillin, behenic alcohol, and n-hexadecanoic acid in EXT; and vanillin and 2-methoxy-4-vinylphenol in SAR.

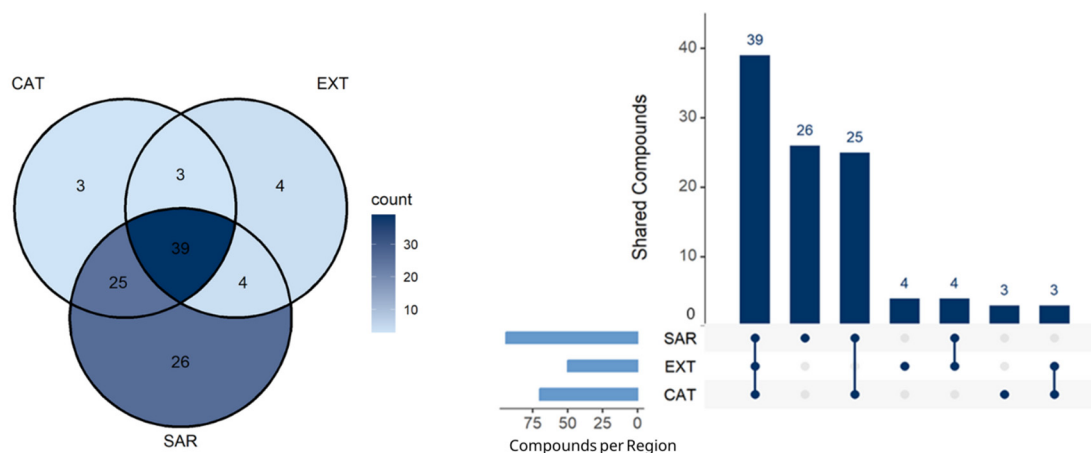


Figure 3. Shared and region-specific volatile compounds across cork samples from Catalonia (CAT), Extremadura (EXT), and Sardinia (SAR). **(Left):** Venn diagram showing the number of VOCs shared between regions, with major abundant compounds annotated. **(Right):** UpSet plot visualising the distribution and intersection of VOCs across the three origins.

We performed a PCA to explore the chemical variability in the cork samples relative to the abundance of each extracted VOC from three distinct geographical origins, focusing on the compounds extracted from these three origins (Figure 4).

In this case, PC1 explained 61.8% of the total variance and PC2 accounted for an additional 38.2%. This made the two-dimensional PCA plot fully representative of the chemical diversity across the samples. The PCA biplot clearly illustrated the differentiation among the three geographical sources. Cork from Extremadura (EXT) clustered on the far right of PC1, associated with compounds such as guaiacol, n-hexadecanoic acid, benzenoacetic acid, and acetophenone. This indicated a distinctive abundance of aliphatic acids and phenolic

esters in these samples. Cork from Catalonia (CAT) was closely associated with orthoacetic acid, 6-methoxy-3-methylbenzofuran, and l-arabinopyranose, suggesting a prevalence of oxygenated furan derivatives and sugar-related compounds. Finally, samples from Sardinia (SAR) were strongly associated with trans-isoeugenol, coniferaldehyde, and vanillin or phenolic compounds often linked to lignin degradation.

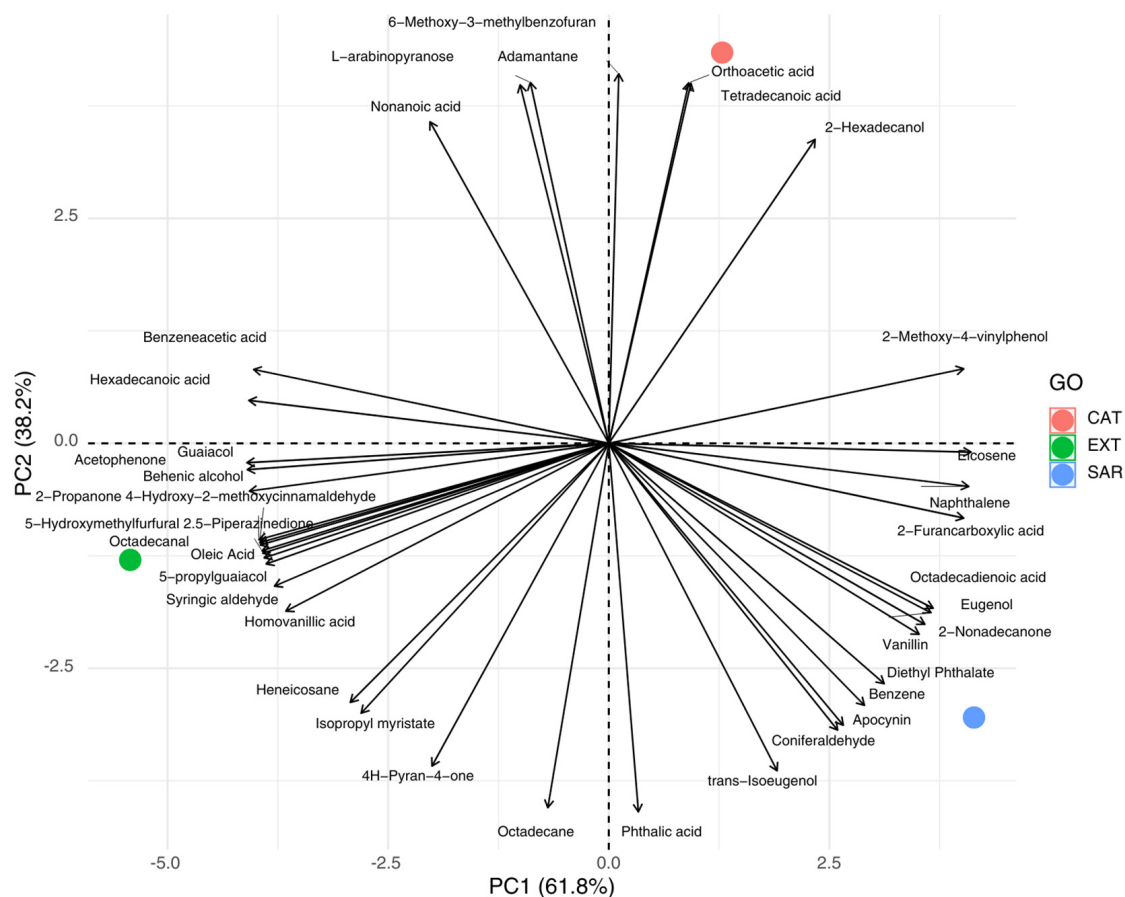


Figure 4. Principal Component Analysis (PCA) of compounds in cork samples by geographic origin. Only VOCs consistently identified across all three geographical origins were included.

Guaiaicol finds extensive use across various industrial sectors, particularly in the production of aromatic compounds such as eugenol or vanillin. In the pharmaceutical field, it plays a crucial role in the synthesis of guaiaicol benzoate (potassium guaiaicol sulfonate), where it is employed as a local anaesthetic or antiseptic, and a few studies on the use of guaiaicol to inhibit plant pathogens have been reported [46]. Benzeacetic acid and other benzoic acid derivatives have antibacterial, antifungal, antialgal, antimutagenic, antisickness, and estrogenic activities and are also widely used as preservatives in drugs, cosmetics, pharmaceuticals, food, and beverages [47]. Acetophenone has emerged as a promising eco-friendly alternative to synthetic pesticides [2]. In addition to its pesticide potential, plant-derived acetophenones are key precursors in pharmaceutical synthesis. For instance, derivatives like apocynin exhibit anti-inflammatory properties without adverse side-effects, making them ideal candidates for drug development [48]. In restricted concentrations, trans-isoeugenol has been used as a functional ingredient in the pharmaceutical, food, and cosmetic industries due to its antimicrobial, anti-inflammatory, analgesic, and antioxidant properties and pleasing aromas and flavours [47]. Finally, coniferaldehyde is an antifungal compound that can be used in specific sectors.

Most of the detected volatile compounds mentioned in Table S1 resulted from the degradation of cork components, such as fatty acid chains (from waxes and suberin), lignin, and aliphatic hydrocarbons derived from extractives and suberin [49]. The diversity of the extracted VOCs suggested the involvement of numerous reactions [11]. Specific methodologies applied to study the profile of cork have utilised solvents at various extraction phases, favouring the depolymerisation of certain cork compounds to address the complexity of cork's chemical composition [8,14,20,31,50]. Extraction at elevated temperatures may lead to compounds with high volatility rather than those with different polarities, as with solvent-based extraction. In this study, efforts were made to obtain the cork profile using a range of temperatures for extraction without considering depolymerisation phases.

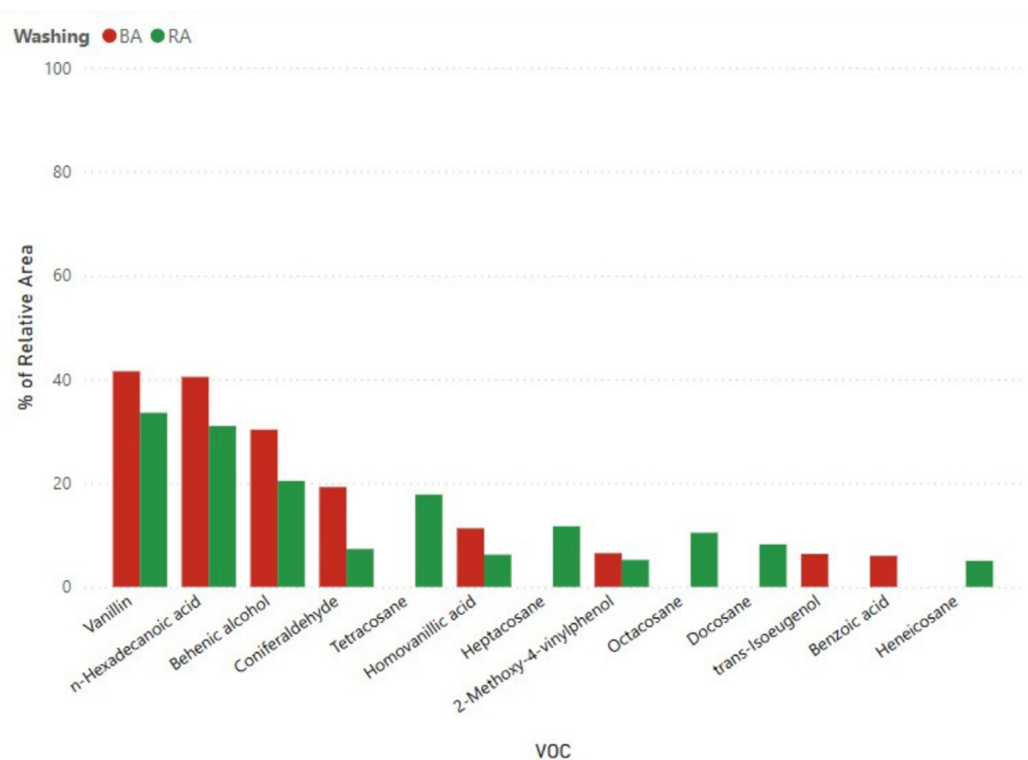
3.3. Volatile Aromatic Profile of Cork Stoppers During the Manufacturing Process

A bar plot of VOCs representing 5% or greater of the relative area of cork stoppers subjected to two washing protocols (RA (spray) and BA (immersion)) was produced (Figure 5A). Compounds from the alkanes family, such as tetracosane, heptacosane, octacosane, docosane, and heneicosane, were only extracted from the RA cork stoppers. On the other hand, lignin-related compounds, such as vanillin, coniferaldehyde, and homovanillic acid, or phenolic compounds, such as behenic alcohol, trans-isoeugenol, or benzoic acid, were more abundant or specific in the BA stoppers.

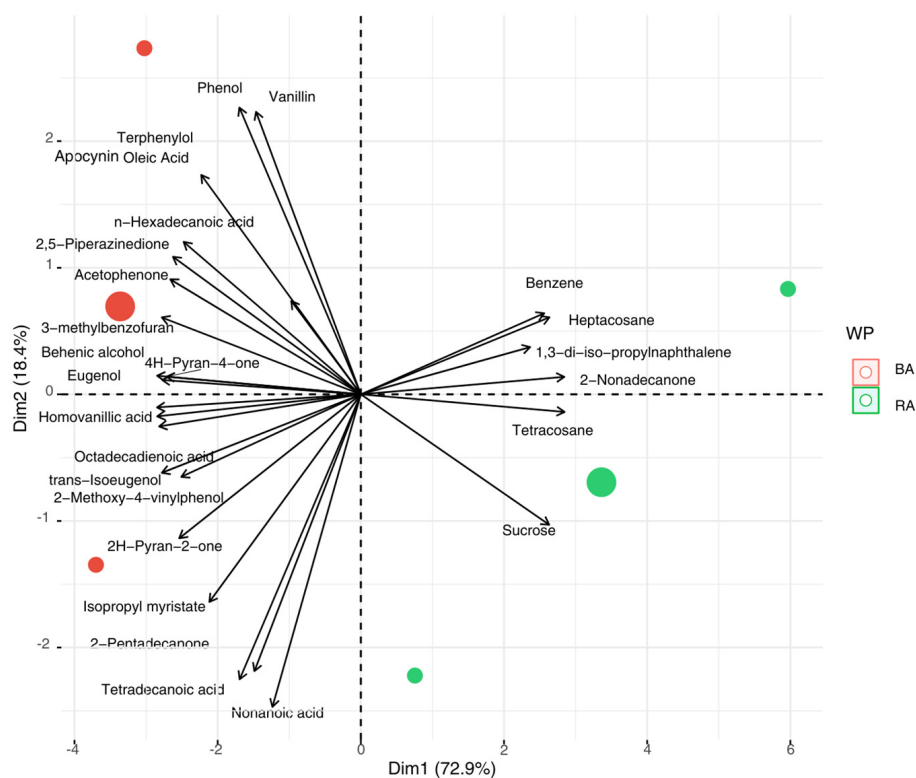
A PCA was conducted to explore the variations in VOC profiles among the cork stoppers subjected to both washing protocols, RA and BA. The first two principal components (PC1 and PC2) explained 72.9% and 18.4% of the total variance, respectively, accounting for 91.3% overall. The biplot (Figure 5B) showed a clear separation between the RA and BA samples along the PC1 axis, suggesting that the washing treatment influenced the VOC composition of the cork stoppers. The BA samples were positioned on the positive side of PC1, while the RA samples were distributed on the negative side, indicating distinct chemical signatures between treatments. VOCs such as 3-methylbenzofuran, 2,5-piperazinedione, n-hexadecanoic acid, and behenic alcohol positively correlated with the BA samples, indicating a higher abundance or stronger association with this washing method. In contrast, compounds such as sucrose, tetracosane, 1,3-diisopropyl naphthalene, and heptacosane showed stronger associations with the RA samples.

The application of a thermal procedure to reduce the presence of potential off-flavours in the cork stoppers was also studied to understand its effect on the aromatic profile of the cork stoppers. VOCs from cork stoppers from Sardinia, washed by a spray and with and without thermal treatment, were compared. A comparative analysis was conducted using a heat-map clustering of the VOCs in cork stoppers with and without TT (Figure 6). Each variable was normalised to generate a clustering map of samples based on a row scale using the relative contents of the extracted 69 VOCs as variables. The distribution frequency of each substance in the sample was shown by a row comparison.

The main VOCs identified—vanillin, n-hexadecanoic acid, and behenic alcohol—stood out due to their consistently high abundance in all samples. Compared with other groups, the cork stoppers with TT exhibited increased levels of ketones such as 2-nonadecanone or acetophenone and a decrease in n-hexadecanoic acid. On the other hand, samples without TT (RA) showed relatively higher contents of alkanes, including tetracosane, heptacosane, octacosane, and docosane, which were not detected in the TT cork stoppers. As shown in Figure 6, hierarchical clustering based on the Euclidean distance grouped the samples into two distinct clusters, clearly separating TT from RA. This suggested a strong influence of thermal treatment on the VOC cork stoppers' profile.



(A)



(B)

Figure 5. Bar plot of VOCs representing 5% or greater of the relative area in RA and BA samples (A). PCA biplot of VOCs in cork stoppers washed using RA (red) and BA (green) procedures (B).

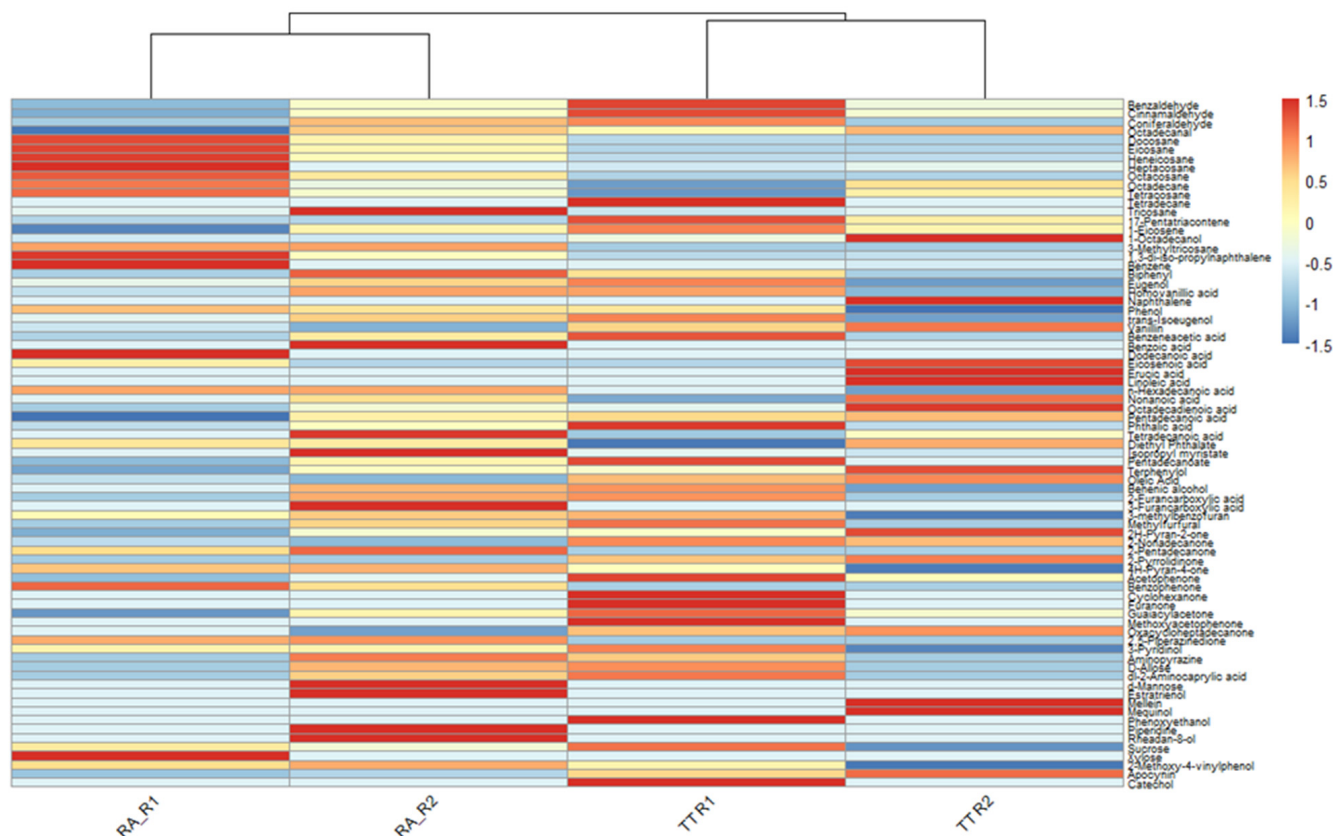


Figure 6. Heat-map clustering of the VOCs in cork stoppers with (TT) and without (RA) thermal treatment.

A PCA was carried out to further explore and visualise the relationships among samples based on their volatile organic compound (VOC) profiles. The analysis was performed using only those commonly detected VOCs in thermally treated (TT) and untreated (RA) samples, ensuring a balanced comparison based on shared chemical information.

The PCA reduced the dimensionality of the dataset while preserving the maximum variance, with the first two principal components (PC1 and PC2) accounting for 52.8% and 32.2% of the total variance, respectively. As shown in the biplot (Figure 7), the two groups of samples were separated along PC1, indicating that thermal treatment significantly influenced the VOC composition. The TT samples were primarily characterised by higher levels of acetophenone, 2-nonadecanone, apocynin, and vanillin, which are known to be formed or enriched during heating processes. In contrast, the RA samples were more closely associated with compounds such as behenic alcohol, 3-pyridinol, sucrose, and trans-isoeugenol. These compounds may reflect the native chemical composition before thermal alteration.

The direction and length of the variable vectors indicated that compounds like acetophenone, 2-methoxy-4-vinylphenol, and docosane contributed most to the variance along PC1, highlighting their discriminative power between sample groups.

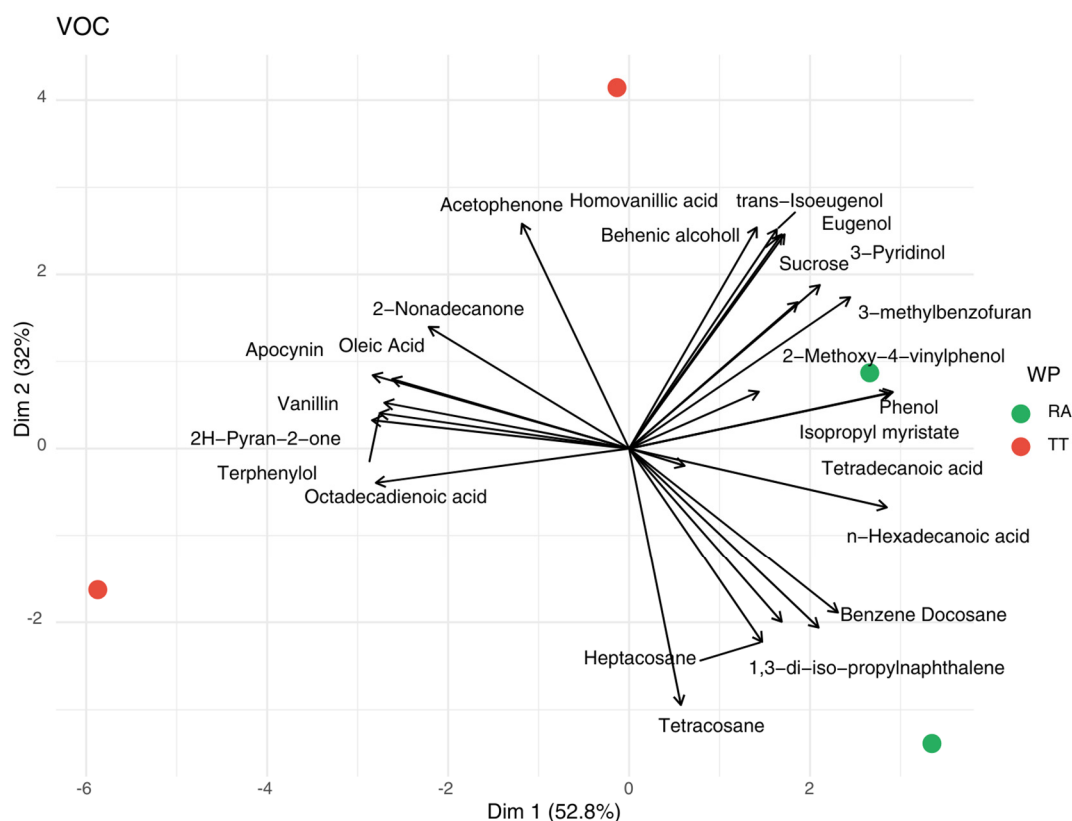


Figure 7. PCA biplot of VOCs in cork stoppers thermally treated or TT (red) and untreated or RA (green) samples.

4. Discussion

This study presents a novel, green, and solvent-free methodology based on thermal desorption coupled to GC-MS to comprehensively analyse volatile organic compounds (VOCs) in cork (*Quercus suber* L.). The method enabled the characterisation of 104 VOCs across samples from different geographical origins and manufacturing stages, revealing significant qualitative and quantitative differences in aromatic profiles.

A statistical analysis confirmed that temperature and geographical origin influenced VOC extraction, with cork from Extremadura yielding the highest overall VOC abundance. Vanillin was the most abundant compound across all origins. Cycloeicosane was highly prevalent in the Catalonia sample as was behenic alcohol in the Extremadura sample and 2-methoxy-4-vinylphenol in the Sardinia samples. Twenty-six VOCs were unique to Sardinia, while twenty-five were shared exclusively between Catalonia and Sardinia. A multivariate analysis showed that the Extremadura samples were associated with carboxylic acids, Catalonia with furan derivatives and sugar-related compounds, and Sardinia with phenolic compounds often linked to lignin degradation.

The aromatic profile of cork stoppers was significantly influenced by the washing method and thermal treatment. Spray-washing resulted in several alkane compounds, while immersion-washing enhanced the abundance of lignin-derived and phenolic compounds such as vanillin, coniferaldehyde, and behenic alcohol. A principal component analysis further confirmed a clear chemical differentiation between both washing protocols, with the RA and BA samples forming distinct clusters based on their VOC composition. Finally, thermal treatment also significantly altered the volatile aromatic profile of the cork stoppers. Compared with untreated samples, the thermally treated stoppers exhibited higher concentrations of specific ketones such as acetophenone and 2-nonadecanone, while the levels of certain alkanes and fatty acids like n-hexadecanoic acid were reduced. Heat-

map clustering and PCA analyses consistently revealed a clear separation between cork stoppers with and without thermal treatment, indicating that thermal processing induces distinct chemical changes.

In summary, this study confirmed that geographical origin, industrial washing procedures, and thermal processing significantly influence the volatile profile of cork. Identifying key aroma-active compounds such as vanillin, guaiacol, and acetophenone highlights the aromatic potential of cork, especially for applications beyond traditional sealing functions. The results demonstrate that immersion- and spray-washing have distinct effects on the retention or removal of specific VOC families, and that thermal treatment can modulate the VOC composition by enhancing certain ketones while reducing fatty acids and alkanes. These findings open new perspectives to valorise cork-derived materials through selective processing.

Future studies should explore the sensory perception of these compounds, quantify their odour activity values, and assess the feasibility of their industrial extraction and application in sectors such as food, cosmetics, and biomedicine.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/pr13051505/s1>, Table S1. List of aromatic profiles of cork samples (CAT, EXT and SAR) susceptible to being extracted by thermal desorption at all selected temperatures.

Author Contributions: Methodology: P.J.; software: P.J.; validation: P.J., R.d.N. and M.V.; formal analysis: P.J.; investigation: P.J.; resources: M.V.; data curation: P.J.; writing—original draft preparation: P.J.; writing—review and editing: R.d.N. and N.F.; visualisation: P.J.; supervision: N.F.; project administration: N.F. and R.d.N. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement: The data presented in this study are available in the article.

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Conflicts of Interest: Author Raquel de Nadal was employed by the Research and Development Department, JVIGAS S.A. The remaining authors declare that the research was conducted in the absence of any commercial or financial relationships that could be construed as a potential conflict of interest.

Abbreviations

The following abbreviations are used in this manuscript:

TD-GC-MS	Thermal Desorption Coupled to Gas Chromatography-Mass Spectrometry
VOC	Volatile Organic Compound
PCA	Principal Component Analysis
CAT	Catalonia
EXT	Extremadura
SAR	Sardinia
BA	Immersion-Washed Cork Stoppers (from Baño or Bath)
RA	Spray-Washed Cork Stoppers (from Rociado or Aspersión)
TT	Thermally Treated Cork Stoppers
NIST	National Institute of Standards and Technology
CAGR	Compound Annual Growth Rate

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