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Charentaise distillation of cognac. Part I: behavior of aroma compounds

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ABSTRACT

The Charentaise distillation plays an essential role in designing cognac aroma by extracting and selectively concentrating aroma compounds from the wine along with ethanol, in addition to promoting compound formation or degradation through different chemical reactions. This traditional mode of distillation still relies heavily on empirical knowledge and the impact of its different parameters on the composition of cognac is not fully elucidated. In this context, this study aimed to broaden the current knowledge on the behavior of aroma compounds throughout the two steps of the Charentaise distillation and to investigate the formation of aroma compounds during the operation, an aspect which is seldom considered. The concentration profiles of 62 aroma compounds were represented over time for a wine and a brouillis distillation in usual scale (25 hL) with recycling. A classification system was then proposed to group compounds based on their volatilities at different ethanol concentrations in the boiling liquid, their concentration profiles and their chemical properties. This could help identify how chemical characteristics of aroma compounds affect their volatilities in hydroalcoholic media during distillation. In addition, several compounds appear to be formed during distillation, most of which are terpenes, norisoprenoids and aldehydes. Finally, to highlight the importance of different compounds to the aroma of freshly distilled cognac, their odor activity values (OAV) in the heart fraction was estimated, revealing isobutanol and (*E*)- β -damascenone to be the most odorant compounds. These results provided additional elements of understanding for different aspects of the Charentaise distillation for the production of cognac, several of which can be transposed, at least in part, to different modes of distillation pertaining to other distilled beverages.

Keywords: cognac; batch distillation; aroma compounds; ethanol; distilled spirits; chemical reactions; volatility.

1. INTRODUCTION

Cognac is a wine spirit produced in the Charente region of France and reputed worldwide for its distinctive aroma bouquet. The intricate blend of fruity, flowery and woody aroma notes is the result of the interplay of hundreds of volatile compounds from different chemical families that are distributed in an ethanol-water matrix. While some of these compounds are native to the grape, the majority of them originates from yeast activity during fermentation or are formed from chemical reactions promoted by distillation conditions (Awad et al., 2017) as well as during aging from further reactions and the extraction of wood constituents (Cantagrel et al., 1995; Caumeil, 1983; Lurton et al., 2012; Tsakiris et al., 2016).

Cognac spirit is typically produced from the distillation of a white wine of the Ugni Blanc grape variety, which is characterized by a pH ~ 3 and an ethanol concentration of 7 - 12% v/v (unit of characterization of alcoholic beverages) and is often distilled with some of its fermentation lees. In accordance with AOC (Controlled Origin Certification) regulations, the wine undergoes a double batch distillation process carried out in copper alembic-type stills with maximal load capacity of 25 hL (2.5 m^3) and heated by a direct flame. Known as Charentaise distillation, the operation requires two successive distillations to obtain a freshly distilled cognac with approximately 70% v/v ethanol: the wine distillation (WD) and the brouillis distillation (BD).

The goal and major challenge of distillation lies in maximizing the extraction of components with pleasant aromas in the freshly distilled cognac while limiting the presence of undesired compounds. To help achieve this goal, the distillate is often divided into different fractions in an operation known as *cutting*. Cutting times might be determined by the cumulated volume of distillate collected, by the ethanol concentration of the distillate (measured with portable alcoholmeters or with density meters installed near the hydrometric port) or, as is most often the case, from an empirical evaluation of the distillate aroma. During the WD, three fractions of distillate are collected separately: the head, the brouillis and the tail, leaving an aqueous residue in the boiler. Similarly, four distillate fractions are typically collected in the BD: the head, the heart, the second and the tail, in addition to the residue. The key fraction resulting from the process is the heart, which corresponds to the freshly distilled cognac that contains up to 73.7% v/v ethanol before being stored in oak barrels for aging for at least two years (Ministère de l'agriculture et de la souveraineté alimentaire, 2022).

Although cutting might help limit the presence of some compounds in the heart to a certain extent, it is only a limited form of control that is highly dependent on the chemical and thermodynamic properties of the system and its constituents and is often subjected to the know-how of the distiller. Furthermore, despite what is often implied in the literature, the fractions other than the brouillis and heart are not discarded, as they contain important amounts of ethanol and aroma compounds that would otherwise be lost. Instead, they undergo a *recycling* operation, in which the heads, tails and second are reintroduced in the process and redistilled in subsequent batches. Typically, heads

and tails are mixed with the wine in the feeds of ensuing WDs and the second is blended with a new batch of brouillis for subsequent BDs.

Despite the averred importance of distillation to cognac aroma, the current scientific knowledge on the intricacies of the process and the impact of its different parameters on the composition of freshly distilled cognac is rather limited. As a result, the set of complex operations it entails still rely heavily on empirical knowledge and traditional practices, which add a high variability to the process. A first approach to unveil the intricacies of the Charentaise distillation was conducted by the National Interprofessional Committee of Cognac more than three decades ago. By plotting the concentrations of aroma compounds as a function of decreasing ABV (alcohol by volume, in % v/v) in the distillate, the group was able to classify 39 aroma compounds into 8 types according to the shapes of their concentration profiles in the WD and the BD, as described in Cantagrel (1989).

A deeper understanding of the spirit distillation process entails considering the vapor-liquid equilibrium (VLE) behavior of the multicomponent system and the physicochemical characteristics of its constituents. From a molecular perspective, the wine and brouillis can be viewed as a strongly hydrogen-bonded water-ethanol matrix in which aroma compounds are highly diluted and thus do not influence the thermal behavior of the system. Thereby, the concentration profiles of aroma compounds in the distillate are essentially driven by the variations in ethanol concentration in the boiler throughout distillation and its effect on the volatility of aroma compounds (Douady et al., 2019; Esteban-Decloux et al., 2022; Puentes, et al., 2018a). This can be expressed by the absolute volatility (K_i), which is the ratio between the molar concentrations of a compound i in the vapor and in the liquid phases at equilibrium for a given composition of the boiling liquid, and the relative volatility in relation to ethanol ($\alpha_{AC/Et}$) and to water ($\alpha_{AC/W}$), the two major components.

Based on this, Puentes et al. (2018a) proposed a systematic classification of aroma compounds into light, intermediate and heavy based on their volatilities in relation to ethanol (light key) and to water (heavy key) over the entire ethanol mole composition of the boiling liquid ($0 \leq x_{Et} \leq 1$). Later, when applying their classification system to a multistage column distillation, the researchers proposed to fine-tune their classification system by considering only the volatilities between $0 \leq x_{Et} \leq 0.1$, which was the ethanol mole range in the boiling liquid for that type of distillation (Puentes et al., 2018b). This approach was applied by Douady et al. (2019) to a pilot-scale batch distillation for the production of cognac. However, the study was limited to a brouillis distillation without recycling and only included 26 aroma compounds, which is quite limited considering the large number of aroma compounds identified in cognac to date (Maarse & Van Den Berg, 1994).

Beyond compound extraction, the high temperatures in the boiler (>80 °C) and the low pH of the wine (3.0-3.5) provide favorable conditions for the occurrence of a wide range of chemical reactions that lead to the formation of certain aroma compounds and the degradation of others. Compound formation during the distillation of alcoholic beverages has been reported in apple brandy (Schreier

et al., 1978), pear brandy (Zierer et al., 2016), cognac (Awad et al., 2017; Galy et al., 2008; Ledauphin et al., 2003), rum (Franitza et al., 2016b), whisky (Masuda & Nishimura, 1980), shochu (Ohta et al., 1991; Yoshizaki et al., 2011) and grape marc distillates (Lukić et al., 2011), although few of these studies exploit the mechanisms behind these reactions in distillation conditions. Awad et al. (2017) listed 20 volatile compounds formed during the Charentaise distillation for the production of cognac, including 2 esters, 3 aldehydes, 12 norisoprenoids and 3 terpenes. For simplification, the study considered a wine and a brouillis distillation with no recycled fractions in the initial load of each distillation and the base wine was stripped from its lees. While the study provides valuable information on the formation of compounds during the Charentaise distillation, the absence of lees and recycling might prevent it from accurately representing reality.

In this context, the present study aimed to employ a more comprehensive approach to understand how different aspects of the Charentaise distillation influence the behavior of volatile aroma compounds and their evolution from the wine to the heart. For this, distillate samples were collected over time from a WD and a BD, in addition to the respective boiler loads and the residues. The analyses were conducted in cooperation with a specialized laboratory in Cognac, during which 99 aroma compounds were analyzed in the samples. The data were exploited in terms of the concentration profiles of aroma compounds during distillation and their repartition between the distillate fractions and the residue, vapor-liquid equilibrium characteristics of the system, the formation and/or degradation of compounds during distillation and the odor impact of different compounds in the heart, expressed by the odor activity value (OAV). Differently from most studies regarding wine spirits, we opted to employ a wine containing some of its fermentation lees and to include recycling in the distillations to generate results that better reflect actual Charentaise distillations.

2. EXPERIMENTAL SECTION

2.1. Raw materials and distillation equipment

The double batch distillation was carried out at the Rechou distillery (Angeac-Champagne, France), in a traditional copper Charentais alembic with a 25 hL load capacity heated by a direct flame. Distillate parameters such as flow rate, density, alcoholic strength and temperature were monitored and recorded every 10 s by a Coriolis flowmeter (Proline Promass E 300, Endress+Hauser) connected to the hydrometer port. Gas pressure and the temperature at different parts of the alembic were also recorded at the same interval. The wine was a white wine from Ugni Blanc grape variety of the Petite Champagne area of the Cognac AOC (registered designation of origin), including part of the residual lees from fermentation and characterized by an alcohol strength of 9.5% v/v and a pH of 3.2.

2.2. Experimental distillation procedure and sampling

The distillation process consisted of two consecutive batch distillations named wine and brouillis distillations (WD and BD, respectively). For the WD, a mixture (2420 L) composed of a wine containing some of its fermentation lees and the recycled heads and tails was loaded into the boiler and distilled for 11 h. The resulting distillate was divided into the head, the brouillis and the tail, which accounted for 99.0% of the ethanol from the load. For the BD, the boiler load consisted of a volume of brouillis equivalent to approximately three WD and the second recycled from a previous batch. The mixture (2490 L) was distilled for 12.5 h to yield four fractions of distillate: the head, the heart, the second and the tail, comprising 99.9% of the initial amount of ethanol. The heads and tails were recycled in the wine of following WDs and the second was mixed with a new batch of brouillis for a subsequent BD. As such, the only fractions of the process that were actually discarded were the aqueous residues that remained in the boiler after each distillation. Approximately 500 mL of sample were collected for every 50 L of distillate obtained in each distillation after their passage through the flowmeter. The mixtures loaded in the boiler for the WD (wine + heads + tails) and the BD (brouillis + second) and the respective residues were also sampled, in addition to average wine and heart samples over the course of four days.

2.3. Analyses of volatile compounds

2.3.1. Chemicals

All chemicals were analytical grade products purchased from Sigma Aldrich and other commercial sources. Demineralized water (resistivity 18.2 M Ω -cm at 25 °C) was obtained from a Milli-Q purification system (Q-Pod, Millipore Waters, France).

2.3.2. Alcohol strength

The alcohol strength of the samples was determined from density measurements at 20 °C using an oscillating tube density meter (Snap 50, Anton Paar). The conversion from density to ABV (in % v/v) was based on the Alcoholometric Tables from the International Organization of Legal Metrology (*International Alcoholometric Tables, OIML R22, 1975*) and considered the samples as ethanol-water mixtures whose density is not influenced by the highly diluted aroma compounds.

2.3.3. Sample preparation

For the brouillis, heart, second and tails, which comprised numerous samples collected over time, average samples were additionally prepared by mixing equal parts of the collected samples for each fraction. These were later used to perform mass balances for each distillation.

For the wine and residue samples, which contain dissolved solids and aroma compounds at rather low concentrations, the chemical analyses were preceded by a laboratory-scale distillation adapted from Awad et al. (2017). The procedure was carried out in a glass rotary evaporator connected to a

vacuum pump and a refrigerating system set to -8°C . The low operating pressure (6 kPa) results in low boiling points of the samples (less than 36°C), allowing to obtain a distillate that is more concentrated in ethanol and aroma compounds while preventing the formation of heat-induced artifacts. During operation, a round bottom flask with 720 g of sample was brought to a boil by a water bath at 40°C and the condensed vapor was collected in a separate flask. The operation was stopped once 120 mL of distillate with an approximate ABV of 40% v/v were collected in the flask. In the case of the residue, which had a very low amount of ethanol, the ABV was adjusted to that of the wine before the distillation procedure. The extraction yield for each compound was established from a mixture of distillate fractions of known composition, which was adjusted to the ethanol concentration of the wine and distilled under the same conditions. They were later used to correct the concentrations of volatile compounds in the treated samples.

All distillate samples were adjusted to an ABV of 40% v/v prior to gas chromatography analyses to prevent matrix effects and minimize measurement variations.

2.3.4. Analysis of major compounds by GC-FID

The major volatile compounds, namely higher alcohols, esters and aldehydes, were quantified using a gas chromatograph (Agilent 7890A) equipped with a flame ionization detector (FID) and an automatic sampler. The injector and detector were both set to 220°C . The detector flame was maintained by hydrogen and compressed air at $30\text{ mL}\cdot\text{min}^{-1}$ and $320\text{ mL}\cdot\text{min}^{-1}$, respectively. An aliquot of $0.4\text{ }\mu\text{L}$ of sample was injected in split mode (split ratio of 25:1) and carried by a hydrogen flow at $1.4\text{ mL}\cdot\text{min}^{-1}$. The stationary phase was a polar CPWax 57 CB fused silica WCOT column (Agilent, $50\text{ m} \times 0.25\text{ mm}$, $0.25\text{ }\mu\text{m}$). 4-methylpentan-2-ol (CAS 108-11-2) was used as the internal standard at $28\text{ g}\cdot\text{L}^{-1}$ in absolute ethanol to minimize system variability between injections ($100\text{ }\mu\text{L}$ per 10 mL of sample). A nitrogen make-up at $25\text{ mL}\cdot\text{min}^{-1}$ was employed to improve signal response. The oven was set to 35°C for the first 5 min, then increased at a linear rate of $4^{\circ}\text{C}\cdot\text{min}^{-1}$ to 220°C and held for 10 min.

2.3.5. Liquid-liquid extraction and analysis by GC-FID

A liquid-liquid extraction using isooctane was employed to quantify C_4 to C_{18} ethyl esters, terpenes and norisoprenoids. For the extraction, 1 g of NaCl and 20 mL of adjusted sample were added to a glass flask and placed in the tray of an automated extractor (GX 271, Gilson). A stock solution containing ethyl nonanoate and ethyl tridecanoate at $5\text{ g}\cdot\text{L}^{-1}$ in absolute ethanol was added as the internal standard ($100\text{ }\mu\text{L}$ per 20 mL of sample). The extraction was done by adding 4 mL of isooctane to the flasks, agitating for 30 s, then left to decant for 30 min. The organic phase was collected and injected in GC vials for analysis.

The extracts were analyzed by GC-FID (Agilent 6890N) equipped with an automatic sampler. The injector and detector were set to 220°C . Hydrogen was the carrier gas at $3.3\text{ mL}\cdot\text{min}^{-1}$. Hydrogen

and compressed air flow for the FID detector were set to 30 mL·min⁻¹ and 400 mL·min⁻¹, respectively. A nitrogen make-up at 28.5 mL·min⁻¹ was employed to improve signal response. An aliquot of 1 µL of extract was injected in splitless mode in a DBWax capillary column (Agilent, 60 m x 0.25 mm, 0.25 µm). The oven temperature was initially at 35 °C for 0.7 min, then raised to 60 °C at a linear rate of 20 °C·min⁻¹ and held for 3.4 min, and finally increased at 4 °C·min⁻¹ to 220 °C and held for 20 min.

2.3.6. Fatty acid extraction and analysis by GC-FID

The extraction of organic fatty acids was conducted in 30 cm long extraction tubes by adding, in order: (1) 3 g of NaCl; (2) 25 mL of adjusted sample; (3) 0.5 mL of a solution of HCl at 5% v/v in demineralized water; (4) 200 µL of a solution of dichloromethane/hexane (50:50 v/v) containing the three internal standards – 4-methylpentanoic acid (CAS 646-07-1, 600 mg·L⁻¹), undecanoic acid (CAS 112-37-8, 1000 mg·L⁻¹) and heptadecanoic acid (CAS 506-12-7, 600 mg·L⁻¹); (5) 4 mL of the extraction solvent, a mixture of dichloromethane/hexane (50:50 v/v). The tubes were then vortexed for 3 min and left to decant for at least 30 min. The organic phase was collected and pipetted in GC vials for analysis.

The extracts were analyzed by GC-FID (Agilent 6890N) equipped with an automatic sampler. The injector and the detector were kept at 250 °C. Hydrogen was the carrier gas at 3.3 mL·min⁻¹. The FID flame was maintained by a flow of hydrogen and compressed air at 30 mL·min⁻¹ and 400 mL·min⁻¹, respectively. 0.5 µL of extract were injected in splitless mode in a polar STABILWAX capillary column (Restek, 30 m x 0.25 mm, 0.25 µm) connected to an RTX-1 column (Restek, 15 m x 0.25 mm, 0.25 µm). The oven temperature was held at 45 °C for 1 min, then raised at 15 °C·min⁻¹ to 80 °C and further raised at 4 °C·min⁻¹ to 250 °C and held for 15 min. Due to the higher complexity of this method, the analysis of fatty acids was conducted in a restricted number of samples. Consequently, the results for acids will only be discussed when pertinent.

2.3.7. Computation of chromatographic data

The chromatographic data were acquired and analyzed using ChemStation software version B.04.03(16) (Agilent). The compounds were identified by comparing their retention times to those of pure standards analyzed under the same conditions. For each analysis, quantifications were based on calibration curves established for each compound from a mixture of reference analytical standards at different concentrations in a hydroalcoholic solution at 40% v/v ethanol. Compounds that were absent from the reference mixture were quantified based on the calibration curves of another compound with similar chemical properties. Limits of quantitation (LOQ) were computed using the signal-to-noise method. Statistical analyses of the results were conducted in Microsoft Excel using one-way ANOVA analysis ($p < 0.05$).

The list of all 99 compounds analyzed and their respective IUPAC names, CAS numbers, LOQ and chemical properties is presented in **Table 1**. For compounds that are commonly denoted by more than one name, the term selected for this study is listed first, and alternative denominations are listed in parenthesis below it. Furthermore, compounds that were absent from the samples or below their limits of detection are italicized.

2.3.8. Calculation of mass balances

Global mass balances were established for each distillation (WD and BD). The mass of the boiler load was calculated from the volume loaded in the alembic multiplied by its density at 20 °C, which was estimated from the measured ABV. This allowed to sidestep any influences that the dry matter dissolved in the wine could have on the mass of the boiler load. The masses of distillate produced during distillation were calculated every 10 s from the volume and density data registered by the Coriolis flowmeter.

For the ethanol mass balances, the amount of ethanol in the boiler load was calculated by multiplying its ABV by the loaded volume, considering that no suspended particles or non-volatile substances were present in the wine. The ethanol content in the distillate was calculated every 10 s by multiplying the average volume of a 10 s interval by the average ABV at that same interval.

For aroma compounds, their masses in each sample were calculated from their concentration in the sample, in mg·L⁻¹, by first dividing the concentration by the sample density, then multiplying the resulting mass concentration by the total sample mass. The mass balances for aroma compounds were established based on their masses in the average distillate fractions. For this, for each distillation (WD and BD) the mass of each aroma compound in the boiler load (in) was compared with the some of its masses in the distillate fractions and residue (out). The repartition of aroma compounds between the distillate fractions and residue was calculated dividing the mass of each fraction (distillate or residue) by the sum of the masses of distillate fractions and the residues.

3. RESULTS AND DISCUSSION

A wine distillation (WD) and a brouillis distillation (BD) for the production of cognac were followed and 500 mL samples were collected for every 50 L of distillate. Additionally, average samples for each distillate cut were constituted from the individual samples. The masses and ethanol content of each load and ensuing distillates and residues are listed in **Table 2**.

Out of the 99 compounds analyzed, only 85 were detected in the samples, including 23 alcohols, 32 esters, 4 aldehydes, 5 norisoprenoids, 5 terpenes, 3 acetals and 13 organic acids.

3.1. Behavior of ethanol and aroma compounds during distillation

The evolution of the mass concentrations of ethanol in the distillate and in the boiler throughout the WD and the BD are shown in **Figure 1**, in which the distillation cuts are represented by dashed vertical lines with their respective ABV values, in %v/v. Given its relatively high volatilities from the beginning of the WD and the BD (8.0 and 3.9 in molar fraction, respectively), ethanol presents a maximal concentration peak in the head fraction, then decreases in concentration as it is extracted from the boiler throughout distillation. The markedly different shapes of the ethanol concentration profiles in the distillate of the WD and the BD result from the different ethanol content in the two boiler loads and the consequent differences in volatilities, which are much higher during most of the WD than in the BD.

To characterize the behavior of aroma compounds during the Charentaise distillation, the concentration profiles of the aroma compounds quantified in this work were plotted as a function of the ABV (% v/v) in the distillate during the WD and the BD, then sorted into light, intermediate and heavy according to their relative volatilities in relation to ethanol ($\alpha_{AC/Et}$) or water ($\alpha_{AC/W}$) in the range of $0 \leq x_{Et} \leq 0.26 \text{ g}\cdot\text{g}^{-1}$, which corresponds to the ethanol concentration in the loads, as proposed by Puentes et al. (2018b).

Within each group, the concentration profiles were compared to those from Cantagrel (1989), with types 1 - 6 for the WD and types 1 - 8 for the BD, as illustrated in **Figure 2**. The results for a few selected compounds are presented in **Figure 3** (light compounds) and **Figure 4** (intermediate and heavy compounds), in which the number above each graph indicates the corresponding type from Cantagrel (1989) and the vertical dashed lines denote the distillate cuts. Compounds whose VLE data are not available were classified based on the resemblance of their concentration profiles to those of compounds with known volatilities.

Light compounds mostly present type 1 profiles in both distillations, or type 1 in the WD and 7 in the BD, as seen for most esters and aldehydes. They present high volatility values throughout the entire Charentaise distillation, especially during the WD. As a result, they are extracted at the very beginning of the distillation and are rapidly depleted from the boiler. In the BD, because their volatilities are lower at the higher ethanol concentration in the boiler load, they tend to present lower concentrations in the head, even if their concentration in the boiler load is higher. Short-chain alcohols classified as light compounds (e.g., propanol, isobutanol) have volatilities that are closer to those of ethanol, presenting a type 4 shape in the WD and type 7 in the BD.

One exception is methanol, whose slightly lower volatilities at the entire distillation place it in the intermediate group. Even if the absolute volatility of methanol is highest in pure water and decreases with the increasing concentration of ethanol, its relative volatility in relation to ethanol goes in the opposite sense, increasing with ethanol concentration. This behavior can be related to

the $\log P$ of methanol (-0.7), which stands between those of ethanol (-0.31) and water (-1.38) (Hansch et al., 1995), as suggested by da Porto et al. (2010).

Intermediate compounds are less volatile than ethanol at the beginning of distillation and gradually increase in volatility as the ethanol content in the boiler decreases. As a result, they are extracted throughout the entire distillation, being mostly present in the brouillis of the WD and in the heart and second of the BD. The intermediate group comprises a large number of compounds with a relatively high heterogeneity regarding their concentration profiles, although most present type 6 profiles in the BD.

Finally, heavy compounds present lower volatilities than water for the entire distillation, being characterized as type 2 in both distillations. Consequently, their concentrations are quite low in the beginning of the first liters of distillate and gradually increase with the decreasing ethanol concentration in the boiler, being highest in the tails. Several of these are partially lost in the residues, as is the case for levo- and meso-butane-2,3-diol. These results are similar to the classification proposed by Douady et al. (2019), although they only considered a BD and a total of 26 compounds.

Given the large number of compounds classified within each group in this study, a significant heterogeneity is observed among them. To address this heterogeneity and provide a more precise classification, we propose a finer multilayered classification system in which light, intermediate and heavy compounds are fragmented into subgroups according to their volatilities throughout distillation (for $0 < x_{\text{Et}} < 0.26 \text{ g}\cdot\text{g}^{-1}$ in the boiling liquid), their concentration profiles in the WD and the BD, and chemical properties such as the octanol/water partition coefficient ($\log P$), the boiling temperature at 101.3 kPa (T_b) and the molecular weight (M), as proposed in **Table 3**. The different compounds quantified in the samples and sorted into the different subgroups are listed in

Table 4. Compounds for which no volatility data were available were classified according to the shape of their concentration profiles and are indicated by an asterisk (*) in

Table 4. For each compound, its respective subgroup and its distribution between the distillate fractions and the residues are listed in **Table 5**.

To further expand the number of compounds in the classification system, some compounds that were not quantified in this study but are known to be present in cognac were tentatively classified based on two criteria: their concentration profiles as proposed in Cantagrel (1989) (signaled in the table by +); their volatility data according to Puentes et al. (2018a) (signaled by #). With this, 83 compounds were considered in our classification system.

With this new system, light compounds are divided into four subgroups. L-I comprises compounds that are highest in concentration in the first liters of distillate and are thus more present in the head fractions (>10% in the head of the BD), with hardly any presence in the tails and residues. Some exceptions to this are 1,1-diethoxyethane and acetaldehyde, which showed an important presence in the residue of the WD (cf § 3.2). This is an atypical behavior for these compounds, which might be linked to the occurrence of oxidative reactions in the residue (e.g. oxidation of ethanol into acetaldehyde) (Lukić et al., 2011; Nykanen, 1986), although the possibility of analytical issues cannot be discarded. The L-I group contains mostly medium-chain esters (<12 C) and short-chain aldehydes (<5 C), both with lower log *P* values (<3.8).

Compounds in the L-II category follow a similar trend, being mostly present in the brouillis and heart, but with a slightly higher presence in the tails than L-I compounds. L-II compounds are essentially medium-chain esters (10-15 C) and non-megastigmane norisoprenoids (e.g., TDN). L-III and L-IV comprise compounds that are a slightly less present in the heads and a little more present in the second and tails. L-III contains longer-chain esters (14-18 C) and alcohols (8-16 C) with higher log *P*, whereas L-IV is constituted by short-chain alcohols (<6 C) with low log *P* values (<2) and volatilities that evolve little throughout distillation.

The differences between light compounds indicate an effect of log *P* on the volatility that is not linear and seems to follow the trends observed by Tsachaki et al. (2006), who suggested that compounds with log *P* between 1.5 and 4 tend to be the most impacted by the variations in ethanol concentration in the liquid, whereas the concentrations of compounds with log *P* lower than 1 or higher than 4 were less affected by ethanol. This could explain, for instance, why groups L-I and L-II, whose components mostly have log *P* values between 1.5 and 4, have higher volatilities than groups L-III and L-IV, whose compounds have log *P* that are either higher than 4.5 or lower than 1.5. In the intermediate categories, I-I contains only methanol, whose volatility is very similar to that of ethanol. As a result, it is present in all distillate fractions. Both I-II and I-III comprise mostly long-chain esters and alcohols with one or more unsaturations, with compounds in I-II having higher log *P* values (4 - 9) and longer carbon chains than those in I-III. Finally, I-IV gathers several compounds categorized as type 6 in the BD but without a clear profile in the WD. They are characterized by medium-chain esters and short-chain aldehydes with multiple unsaturations, as well as carboxylic

acids with 4 to 12 carbons. Intermediates from I-II to I-IV all present a similar inverted-v shape in the BD whose concentration peaks appear at different moments of the BD: in the heart for I-II, between the heart and second for I-III and near the tail cut for I-IV. This is a clear reflex of their differences in volatilities. Group I-IV can be considered as a transition group between intermediate and heavy compounds, since its compounds tend to be more concentrated in the later stages of distillation, between the second and tail fractions.

Finally, the group of heavy compounds is composed of aroma compounds with increasing concentrations throughout the entire distillation, presenting a concentration peak in the final liters of distillate. These are essentially alcohols presenting more than one oxygen and short-chain carboxylic acids (2-3 C), being characterized by extremely low $\log P$ values (-0.9 to 0.3). Their volatilities vary minimally with changes in the ethanol concentration of the boiling liquid.

By grouping the light, intermediate and heavy compounds into the proposed subgroups according to their commonalities, it is clear that the highest influence on the behavior of aroma compounds during distillation is from their absolute and relative volatilities (K_{AC} and $\alpha_{AC/Et}$), as has been reported in the literature (Esteban-Decloux et al., 2022). Additionally, the compounds in each subgroup appear to share some structural and physical-chemical characteristics, suggesting that parameters such as the chemical group, the chain length and conformation, the molecular weight and the $\log P$ value might affect the volatilization of aroma compounds. This has been evidenced for the release of aroma compounds during the consumption of distilled beverages (Ickes & Cadwallader, 2017; Yu et al., 2023), but further research is needed to better understand in what manner and to what extent these different properties contribute to the behavior of aroma compounds during distillation.

Although it has been repeatedly suggested in the literature that the boiling temperature of the pure component at 101.3 kPa is one of the key factors driving the volatilization of compounds during distillation (Alcarde et al., 2010; Guymon, 1974; Léauté, 1990; Silva et al., 2000), not enough evidence has been provided in this sense and the data presented in this study indicate otherwise. For instance, several esters with boiling points above 200 °C are more concentrated in the beginning of the distillation, whereas compounds such as levo- and meso-butane-2,3-diol, whose T_b are around 77 °C, have low concentrations in the beginning of distillation and present a peak in concentration in the tails.

3.2. Mass balances for ethanol and aroma compounds

Mass balances were computed for the different compounds from their masses in the beginning and at the end of the wine and brouillis distillations as described in the experimental section. An out/in ratio was then established for each aroma compound in the WD and in the BD by dividing its summed masses in the distillate fractions and residue by its mass in the load. Compounds with an out/in ratio of 1.5 or higher are considered as formed, whereas those with a ratio lower than 0.66

are deemed as degraded. Compounds that were below their LOQ in the wine or brouillis but were present at the end of distillation with a mass of at least 0.05 g are denoted by +++.

Initial and final masses of the different compounds and their corresponding out/in ratios are listed in Table 5. Compounds such as benzyl alcohol, levo-butane-2,3-diol, meso-butane-2,3-diol, isobutyl acetate and 1,1,3-triethoxypropane were not quantifiable in the load of the WD and are thus not included in the table.

The results showed that most of the compound formation occurred in the WD. This is in part due to the presence in the wine of non-volatile precursors that do not distill into the brouillis and are thus not present in the BD. Similar results were observed by Awad et al. (2017), who highlighted the formation of 20 aroma compounds during the Charentaise distillation for the production of cognac. In this work, 31 compounds had their masses increased during the WD, nine of which were listed by Awad et al. (2017), whereas only 13 compounds increased in quantity during the BD, including two reported by Awad et al. (2017). In addition, 5 compounds were significantly degraded in the WD and 7 in the BD, an aspect which was not considered in the study by Awad et al. (2017) nor in other studies in the literature.

The mass balance results and the chemical reactions that could explain the formation or degradation observed for some compounds are discussed in depth for each chemical family. The out/in ratios for some compounds are mentioned in parenthesis.

Alcohols

Alcohols are mostly formed during fermentation, from the degradation of sugars, the transamination of amino acids or from the reduction of aldehydes by yeast (Guymon, 1974; Nykänen & Nykänen, 1991). During distillation, they remained essentially unchanged, presenting out/in ratios close to 1 for both the WD and the BD. Only three alcohols increased in quantity during the WD: dodecanol (1.9), tetradecanol (3.2) and hexadecanol (+++). They might have been formed from the hydrolysis of the corresponding esters (ethyl dodecanoate, ethyl tetradecanoate and ethyl hexadecanoate) as the wine was depleted of ethanol during distillation, since a more aqueous medium could rapidly shift the equilibrium of the esterification reaction to favor ester hydrolyses (de Rijke & ter Heide, 1983).

Esters

Although esters are typically formed during fermentation (Kelly et al., 2023), several of the esters quantified in this study were present in significantly higher amount in the distillate of the WD, including isoamyl dodecanoate (12.2), ethyl tetradecanoate (8.7), ethyl hexadecanoate (7.8), isoamyl decanoate (4.6), ethyl linoleate (4.4), ethyl oleate (4.3), ethyl linolenate (4.2), isobutyl decanoate (3.2), ethyl dodecanoate (2.8), ethyl octadecanoate (2.7), methyl salicylate (2.3), 2-phenylethyl octanoate (1.9) and ethyl formate (+++). This increased presence of esters at the end of

distillation can be related to the presence of yeast lees in the wine, as suggested in the literature. Distilling in the presence of lees has long been associated with an increased amount of esters in freshly distilled spirits when compared to the wine and an enhanced floral aroma that is typically attributed to this chemical family (Cantagrel, 1989; Guymon, 1974; Silva et al., 2000; Sourisseau, 2002). Some of the esters whose amounts are believed to increase by distilling with lees are ethyl octanoate, ethyl decanoate, ethyl dodecanoate, isoamyl octanoate, isoamyl decanoate, isoamyl dodecanoate, 2-phenylethyl octanoate and 2-phenylethyl decanoate (Cantagrel, 1989; Caumeil, 1983; Maarse & van den Berg, 1994; Suomalainen, 1981).

Ester formation could potentially be associated with the esterification of organic acids in the presence of alcohols. However, although esterification reactions are known to occur during the fermentation and the aging steps (Cole & Noble, 2003; Franitza et al., 2016b; Kelly et al., 2023), the decrease in concentration for ethanol and other alcohols over the course of distillation is unfavorable for esterification.

Since the hypothesis of ester formation does not appear viable, another explanation for the high out/in ratio observed for some esters could be a release of ester from the lees. Long-chain esters tend to be adsorbed on yeast cell walls after fermentation due to a higher lipid solubility, being gradually released into the hydroalcoholic medium with increasing temperature during distillation (Suomalainen, 1981). Moreover, distillation conditions are prone to disrupt the yeast cell structure, thus releasing additional esters that were initially trapped in the cells (Caumeil, 1983; Guymon, 1974; Suomalainen, 1981). In this study, the wine samples underwent a low-pressure distillation (6 kPa) before analyses whose low temperatures (<36 °C) might not have sufficed to release esters from the lees. As a result, the masses of some of the esters might have been underestimated in the wine, leading to overly large out/in ratios.

To verify this hypothesis, three samples of the same wine with lees having undergone each a different pre-treatment were submitted to low-pressure distillations as described in subsection 2.3.3 and the resulting distillates were analyzed by GC-FID as described in the methodology section. The different samples consisted of: (1) Wine with lees (WL) – the untreated wine with its lees; (2) Clear wine (CW) – the wine separated from its lees after centrifugation (4000g, 4 °C, 15 min); (3) Wine with disrupted lees (WDL) – the wine with its lees after an ultrasound treatment (20 kHz, 90% amplitude, 10 min) during which the wine was kept in an ice bath to regulate its temperature. The results (data not shown) reinforce the notion that wines distilled with their lees result in distillates with more esters, namely ethyl octanoate, ethyl decanoate, ethyl dodecanoate, ethyl tetradecanoate, isoamyl octanoate, isoamyl decanoate, isoamyl dodecanoate, 2-phenylethyl octanoate, ethyl 9-decenoate. Furthermore, a comparison between WL and WDL indicates that the yeast cell disruption from the ultrasound treatment improved the extraction of some esters (i.e., isoamyl acetate, ethyl 2- and 3-methylbutanoate, ethyl tetradecanoate, ethyl hexadecanoate, ethyl octadecanoate, farnesyl acetate, ethyl oleate, ethyl linoleate and ethyl linolenate) during the low-

pressure distillations. These preliminary results appear to confirm that some esters (especially long-chain esters) are indeed trapped in the yeast cells and that the low-pressure distillations alone are not adapted to fully extract them from the wine into the distillate. As suggested above, this could explain a substantial part of the apparent ester formation during the Charentaise distillations in this study, although the matter is worth investigating more deeply in the future.

On another note, some esters present low out/in ratios for the WD, suggesting that they are partially lost during the process. This is the case for ethyl 2-methylbutanoate (0.53), ethyl 3-methylbutanoate (0.65), ethyl hexanoate (0.66) and hexyl acetate (0.66), which are mostly found in the head (55-69%). Similarly, low ratios were observed during the BD for ethyl octanoate (0.61), ethyl decanoate (0.52), ethyl dodecanoate (0.59) and isoamyl dodecanoate (0.61). This decrease observed for some esters is quite surprising since several of the esters whose masses are expected to be increased in the presence of lees, as seen above, appear to have been partially lost in the process. This loss might be due to temperature-catalyzed hydrolyses, yielding the corresponding carboxylic acids (in the case of ethyl esters) or higher alcohols (for acetate esters), or from the saponification of the esters with copper ions from the alembic walls (Schaefer & Timmer, 1970). Ester hydrolyses are pH dependent reactions whose rates are reportedly higher for acetate esters and long-chain ethyl esters (Cole & Noble, 2003; Ramey & Ough, 1980).

Aldehydes

Although at least 14 aldehydes have been identified in cognac to date (Ledauphin et al., 2006), only four aldehydes were quantified in this study due to the choice of the analytical methods, which were not adapted to quantify trace aldehydes that would have required a derivatization step before analysis, as in Awad et al. (2017). All four aldehydes showed a significant increase in quantity during the WD, in which the out/in ratios of furfural, isobutanal, acetaldehyde and benzaldehyde were 6.6, 5.4, 4.8 and 3.3, respectively. This increase is reflected in oddly-shaped concentration profiles of acetaldehyde and isobutanal in the WD. Due to their high volatilities throughout the distillation, acetaldehyde and isobutanal have high concentrations in the head fraction and would normally gradually decrease in concentration during distillation due to exhaustion from the boiler. However, at approximately 4 hours of distillation a new increase in concentration is observed for both compounds, likely attributed to a formation throughout the rest of the distillation time. As a result, both compounds are present in all distillate fractions. Isobutanal, acetaldehyde and benzaldehyde are Strecker aldehydes formed from the reactions of α -amino acids with carbonyl compounds, resulting in an aldehyde that is one carbon shorter than its amino acid precursor (Weenen & van der Ven, 2001). This formation is evidenced to be more pronounced for the double distillation than for other distillation systems, likely influenced by the long distillation times (Madrera et al., 2003). Acetaldehyde is reportedly formed from cysteine and alanine, whereas isobutanal derives from valine and glyoxal and benzaldehyde stems from isoleucine (Christoph & Bauer-Christoph, 2007; Galy et al., 2008; Nykanen, 1986).

While furfural was also quantified in all fractions, it was more concentrated towards the end of the distillation and was partially evacuated in the residue, as seen in Figure 4. A similar behavior was observed in other studies for different distilled beverages (Awad et al., 2017; Ikari & Kubo, 1975; Matias-Guiu et al., 2016; Prado-Ramírez et al., 2005; Xiang et al., 2020). Furfural is a Maillard reaction product that is formed during spirit distillation from heat-activated degradations of residual pentoses from the fermentation stage (Ikari & Kubo, 1975); the reaction appears to be greatly impacted by the pH, the temperature, the amount of lees and the distillation method (Joslyn & Amerine, 1941; Léauté, 1990; Miller, 2019; Sourisseau, 2002; Tsakiris et al., 2016). These thermal degradations are highly influenced by the distillation temperatures, which can be as high as 102 °C at the end of distillation.

For the BD, in which no residual sugars were present in the load, the amounts of aldehydes remained steady and only benzaldehyde was slightly raised (out/in = 1.8). This apparent additional increase for benzaldehyde was unexpected as no evidence was found in the literature to support a potential formation in the BD. Thus, the possibility of analytical error cannot be discarded.

Norisoprenoids and terpenes

Norisoprenoids and terpenes are valued for their important contribution to the aroma of cognac and other distilled spirits (Wang et al., 2019). All five norisoprenoids and two of three terpenes analyzed in this work increased in quantity during the WD: vitispirane 2 (7.4), vitispirane 1 (4.2), TDN (3.8), (*E*)- β -damascenone (2.8), TPB (+++), (*Z*)-linalool oxide (3.7), α -terpineol (3.5) and linalool (1.7). The majority of those were listed in the study by Awad et al. (2017). The two chemical families are known to be present in the wine both as volatile aglycones and in non-volatile glycosylated form, the latter being up to 9 times more predominant (Gunata et al., 1985; Park & Noble, 1993). The high temperatures and low pH of wine distillation are ideal conditions for acid hydrolyses of aroma glycosides, which result in a gradual liberation of odor-active terpenes and norisoprenoids from the β -D-glucose moieties (Dziadas & Jeleń, 2016; Skouroumounis & Sefton, 2000; Waterhouse et al., 2016). While glycosylated compounds are non-volatile, more water-soluble and less reactive than their free forms, the hydrolytically released aglycones pass into the vapor phase and tend to enhance the fruity and floral aroma of the distillate (Cole & Noble, 2003; López et al., 2004; Strauss & Williams, 1983). The long distillation times (over 10 h) likely suffice to hydrolyze most glycosides, and any remaining glycoside will be evacuated in the residue and thus not pass into the brouillis. This would explain the nearly steady amounts of terpenes and norisoprenoids during the BD.

In some cases, aroma compounds are not directly formed from the glycoside hydrolysis; instead, they originate from further acid-catalyzed molecular rearrangements of released aglycones that take place to form more thermodynamically stable compounds (Carrau et al., 2008; Ohta et al., 1991; Waterhouse et al., 2016). This is particularly relevant in the formation of norisoprenoids, which are known to derive from multiple precursors (Hjelmeland & Ebeler, 2015; Kinoshita et al., 2010),

including glycosides, carotenoids and other volatile compounds. Molecular rearrangements could also account for the additional formation of TPB during the BD, which has been traced to the rearrangement of actinidol under acidic conditions (Cox et al., 2005). Although actinidol was not analyzed in this study, four actinidols have been previously quantified in freshly distilled cognac (Awad et al., 2017). The formation of terpenes and norisoprenoids during distillation has been evidenced in other works (Awad et al., 2017; Franitza et al., 2016b; Masuda & Nishimura, 1980; Zierer et al., 2016), which also include the terpenes hotrienol and myrcenol and the norisoprenoids Riesling acetal, actinidol, 4-(2,3,6-trimethylphenyl)-butan-2-one (TMPBA) and 4-(2,3,6-trimethylphenyl)-3-butan-2-one (TMPBE), all of which were not analyzed in this work. Finally, the concentration of terpenes also seems to be influenced by the presence of yeast lees, even if to a smaller extent than esters; terpenes adsorbed by yeast cells in the wine would be released along with esters during distillation (Hjelmeland & Ebeler, 2015; Thibaud et al., 2020).

Given the complexity of the formation pathways for terpenes and norisoprenoids, tracing an odorant aglycone to a specific volatile or non-volatile precursor can be a challenging task. Based on the current knowledge in the subject, potential precursors for the formation of the terpenes and norisoprenoids listed in this work are: for TDN, violaxanthin (Winterhalter & Gök, 2013), oxo- α -ionone (Gök et al., 2022) and Riesling acetal (Winterhalter, 1991); for (*E*)- β -damascenone, neoxanthin (Bezman et al., 2005) and allenic triol (Baderschneider et al., 1997; Skouroumounis et al., 1992); for (*Z*)-linalool oxide, linalool (Rettberg et al., 2012); for α -terpineol, α -terpenyl- β -D glucopyranoside, linalyl- and neryl- β -D glucopyranoside, linalool or nerol (Ohta et al., 1991; Williams et al., 1982).

Acetals

Acetal formation during distillation is attributed to reversible addition reactions between aldehydes and alcohols to form a hemiacetal and subsequent condensation by another alcohol. The reaction is favored by the acid environment of the WD and catalyzed by the presence of hydrogen ions (H^+) (Guymon, 1974), and appears to be particularly significant in directly fired stills (Coelho et al., 2020). Acetals formed during the WD were 1,1-diethoxyethane (3.2) and 1,1-diethoxyisobutane (2.0). The first is the major acetal in distilled spirits, being formed from the reaction of ethanol and acetaldehyde. The other, 1,1-diethoxyisobutane, likely originates from the acetalization of ethanol and isobutanol (2-methylpropanal) (Joslyn & Amerine, 1941; Thibaud et al., 2019). Due to the reversibility of the reaction, the decreasing ethanol concentration in the boiler during distillation could spur the reverse reaction, leading to the hydrolysis of acetals into their corresponding aldehydes (Misselhorn, 1975). This might have been the case during the BD, since all three acetals presented low out/in ratios (0.12 - 0.53), although no formation was observed for isobutanol and acetaldehyde during the BD.

These results corroborate several of the findings of the study by Awad et al. (2017) and further expand the list of compounds formed during the Charentaise distillation. While in that study the

authors distilled a clear wine and chose to not consider the recycling of distillate fractions, here we distilled a wine with part of its lees and included recycled fractions in our boiler loads to be closer to reality. The presence of lees in this study might explain the substantially higher number of esters whose masses seemingly increased during distillation.

3.3. Changes in composition from the wine to the heart

To illustrate how the Charentaise distillation with recycling affects the concentrations of aroma compounds from the wine to the heart, the experimental mass concentrations of aroma compounds in terms of ethanol (g/g_{Et}) were compared in wines and hearts sampled from the distillery on four consecutive days, as depicted in **Figure 5**. The concentrations of alcohols are quite comparable in the wines and hearts of each day, with small variations due to external factors. This corroborates the previously discussed results, which indicated that the masses of alcohols remained mostly steady during distillation. A similar trend for alcohols was observed by Esteban-Decloux et al. (2021) over several consecutive cider distillations. One exception is 2-phenylethanol, which, as previously stated and reported by Douady et al. (2019), is partially lost in the residue and is thus less present in the hearts than in the wines.

Contrastingly, esters, terpenes and norisoprenoids, which have been shown to increase in amount during distillation, are substantially more concentrated in the hearts than in the wines. This is particularly true for long-chain esters, whose significantly higher concentrations were likely a result of a liberation from yeast cells during distillation, as suggested in the literature (Nykänen & Nykänen, 1991; Suomalainen, 1981) and confirmed by preliminary studies detailed in the previous subsection. Additionally, for several esters, their concentration in the hearts decreases from one day to another, despite having relatively stable concentrations in the four wine samples. This could be explained by the fact that these compounds are present only in small amounts in the recycled fractions and are partially lost in the residue, as previously reported in the literature (Douady et al., 2019).

Finally, compounds whose concentrations in the wines are significantly higher than in the hearts are those with substantial losses in the residue. This is the case for 2-phenylethanol, ethyl lactate, most acids and, to a smaller extent, diethyl succinate. Nevertheless, it must be noted that the hearts collected in this study originate from large-scale (25 hL) distillations in a distillery environment and are thus liable to small variations in the operation parameters from one day to another.

3.4. Odor-active compounds in freshly distilled cognac

Not all volatile compounds constituting the heart fraction truly contribute to its overall aroma. In order to exert an olfactive impact, aroma compounds must be present in the liquid at concentrations above their odor perception threshold, which is the minimal concentration of a compound at which its odor can be perceived in a given matrix. The actual contribution of volatile compounds to the

aroma of the heart can be estimated by their odor activity values (OAV), which correspond to their concentration in the heart divided by their perception threshold.

The OAVs of select aroma compounds in the heart are listed in **Table 6** with their experimental concentrations in the heart, their perception thresholds from the literature and their characteristic odor notes. When calculating OAVs, it is paramount to select thresholds that were measured in a matrix that is similar to the sample, since perception threshold values in ethanol-water mixtures are highly influenced by the ethanol concentration (Fiches et al., 2014; Ickes & Cadwallader, 2017; le Berre et al., 2007; Lee et al., 2001). Thus, given that distilled spirits are typically commercialized with approximately 40% v/v of ethanol, only perception thresholds from the literature that were measured in hydroalcoholic solutions close to that ethanol concentration were considered to estimate the OAVs.

Based on these results, the compounds with the highest influence on the aroma of the freshly distilled cognac were, in decreasing order of importance, isobutanal, (*E*)- β -damascenone, ethyl 2-methylbutanoate, ethyl hexanoate, ethyl butyrate, ethyl octanoate, ethyl decanoate, ethyl 3-methylbutanoate, ethyl acetate, octanoic acid, ethyl linoleate, 3-methylbutan-1-ol, 3-methylbutanoic acid, isobutanol and ethyl dodecanoate, all of which had an OAV higher than 10. Other studies have considered these compounds to play a key role in the intricate aroma of cognac (Ferrari et al., 2004; Lurton et al., 2012; Uselmann & Schieberle, 2015). They have also been shown to contribute to the aroma profile of other distilled beverages such as bourbon whisky (Poisson & Schieberle, 2008), rum (Pino et al., 2012) and pear distillates (Zierer et al., 2016).

The estimation of OAVs is limited by the availability of threshold data in hydroalcoholic mixtures. As such, there might be other compounds that contribute to cognac aroma but are not listed as highly odorant compounds in this work and in the literature due to a lack of threshold data.

It is important to keep in mind that perception threshold data are liable to significant variations depending on the method selected for their measurement, and they seldom consider chemical and perceptual interactions between compounds in a mixture and the influence of the food matrix on compound retention and release. Furthermore, in some cases perceptive interactions between aroma compounds might enhance or suppress the olfactive impact of certain compounds. In such cases, odorants could exert an aroma impact even if their OAVs are below 1 and, conversely, the contribution of compounds with high OAVs to aroma can be weakened or even suppressed (Grosch, 2001; Qin et al., 2022). For instance, (*E*)- β -damascenone and (*Z*)-whisky lactone were found to enhance the perception of a mix of terpenes in aged cognac (Thibaud et al., 2020). Hence, OAVs should be considered only as indicative values to estimate the olfactive importance of different compounds in samples with a similar matrix.

4. CONCLUSIONS

This study followed a wine distillation (WD) and a brouillis distillation (BD) for the production of freshly distilled cognac on a large scale (25 hL). As is usual in cognac distilleries, the wine was distilled with its lees and distillate fractions from previous distillations were recycled in the loads of the WD and BD.

The concentration profiles of 62 aroma compounds were determined over time for both distillations, several of which were followed for the first time. A mass balance allowed to determine the repartition of compounds between the distillate fractions and the residue. Compounds were then sorted between light, intermediate and heavy subgroups according to their volatilities in hydroalcoholic media, their concentration profiles during distillation and their chemical characteristics. In future works, the influence of chemical properties such as the molecular structure and the octanol/water partition coefficient on the behavior of aroma compounds during distillation could be investigated more in depth. A deeper knowledge on this aspect could provide a better understanding of the behavior of aroma compounds during distillation and lead to a more comprehensive classification system.

Furthermore, a comparison of the mass of compounds loaded in the alembic and their masses in the resulting distillate and residue indicated that at least 30 compounds have seemingly increased in mass during the process. Most of these were esters, terpenes, norisoprenoids and aldehydes. Terpenes, norisoprenoids and aldehydes were likely formed from the degradation of non-volatile precursors or from rearrangements of other volatile components. Esters, on the other hand, are believed to have been released from the wine lees due to the high temperatures of distillation. The majority of these formations were restricted to the WD, since most of the precursors are non-volatile and thus remain in the wine. The reactions and/or potential precursors that are likely responsible for compound formation during distillation were extensively discussed based on the scattered literature data from the last few decades. Given the scarcity of this information in the literature, more studies need to be conducted on the formation and/or degradation of aroma compounds in distillation conditions.

Finally, the evolution of the mass concentrations of aroma compounds from the wine to the freshly distilled cognac was evaluated, corroborating the results discussed in the first two sections of this study. To highlight the contribution of the different volatile compounds to the aroma of freshly distilled cognac, their odor activity values (OAV) were calculated based on odor threshold data from the literature. The most odorant compounds were shown to be isobutanal, (*E*)- β -damascenone, ethyl 2-methylbutanoate, ethyl hexanoate and ethyl butyrate. This list is not definitive as is limited to compounds whose odor threshold at 40% v/v ethanol is known, and a more comprehensive list would require measuring the log *P* of other compounds in these conditions.

These results provided a more thorough understanding of the behavior of aroma compounds during the Charentaise distillation, including the concentration profiles of compounds seldom mentioned in the literature and a list of newly-formed compounds that complements previously published

works. These experimental results will be further exploited in our upcoming study which employs computer simulation tools to explain how the recycling of distillate fractions impacts the composition of freshly distilled cognac.

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Notes

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CRediT authorship contribution statement

G.Z. Methodology, Formal analysis, Investigation, Writing - Original Draft, Writing - Review & Editing, Visualization. **P.G.** Writing - Review & Editing, Supervision. **V.A.** Writing - Review & Editing, Supervision. **S.V.** Writing - Review & Editing, Supervision. **V.W.** Methodology, Writing - Review & Editing. **M.E.D.** Conceptualization, Methodology, Formal analysis, Writing - Review & Editing, Supervision, Funding acquisition.

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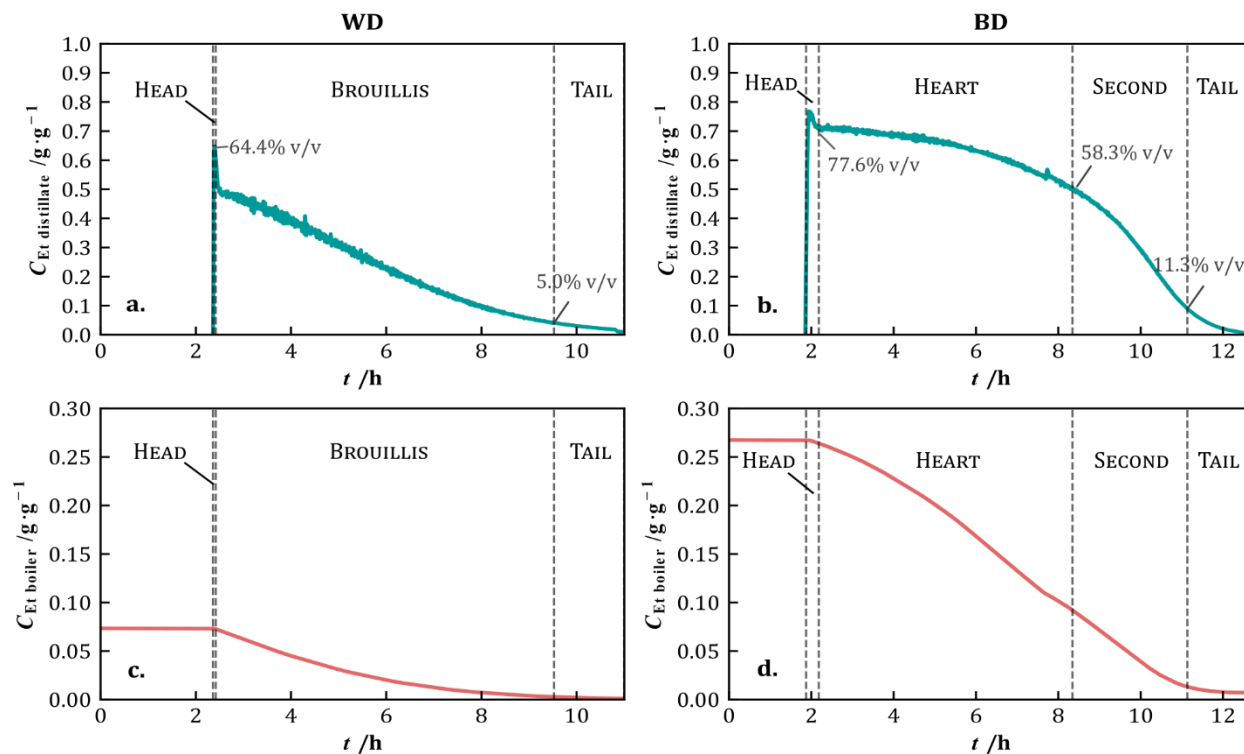


Figure 1. Ethanol concentration profiles in the distillate (a,b) and in the boiler (c,d) during the WD and the BD.

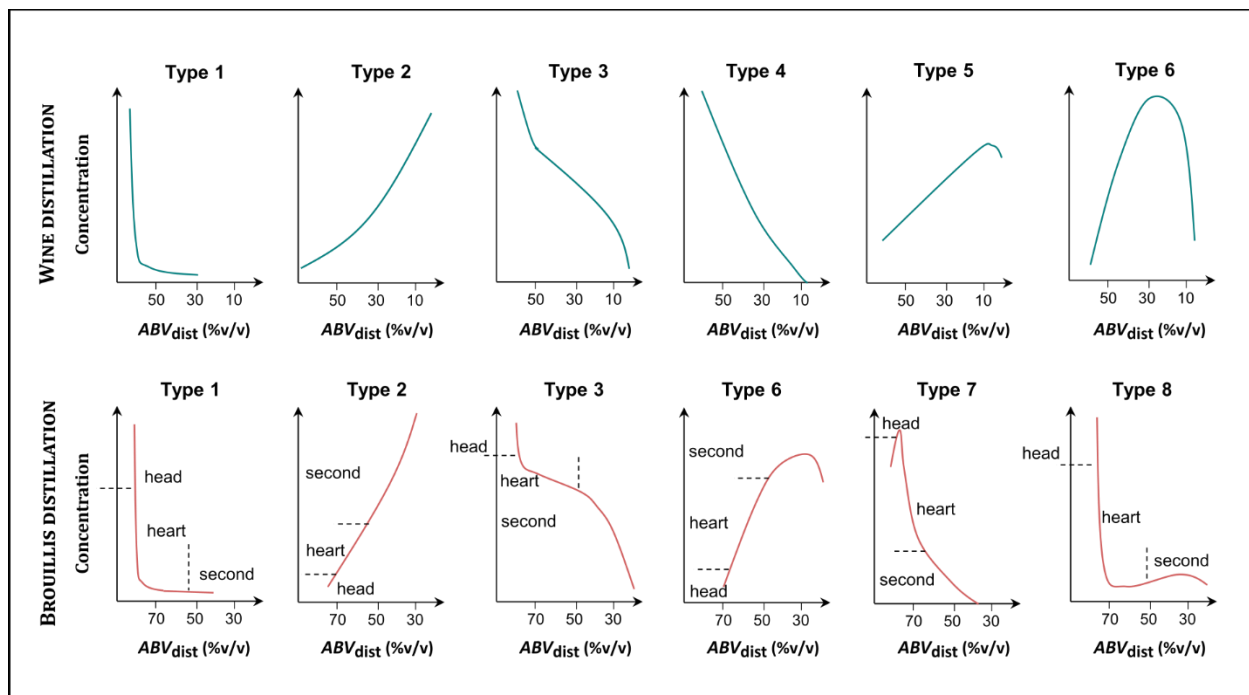


Figure 2. Concentration profiles as a function of decreasing ethanol concentration (in % v/v) in the distillate proposed by Cantagrel (1989) for the wine and brouillis distillations. Adapted from Douady et al. (2019).

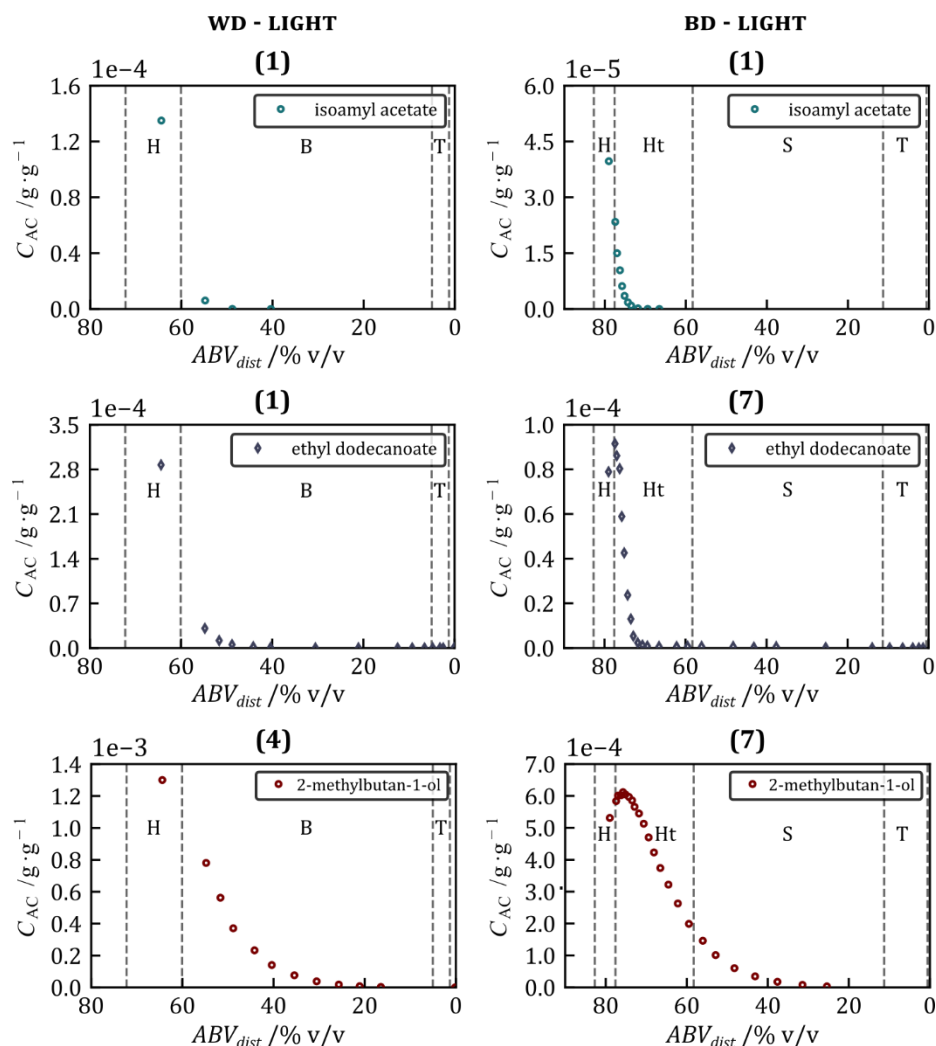


Figure 3. Concentration profiles of light aroma compounds as a function of decreasing ethanol concentration (in % v/v) in the distillate during the WD and the BD. For each graph, the corresponding profile shape from Cantagrel's classification is indicated in bold in parenthesis on top of the graph. Distillate cuts are represented by vertical dashed lines: H, head; B, brouillis; T, tail; Ht, heart; S, second.

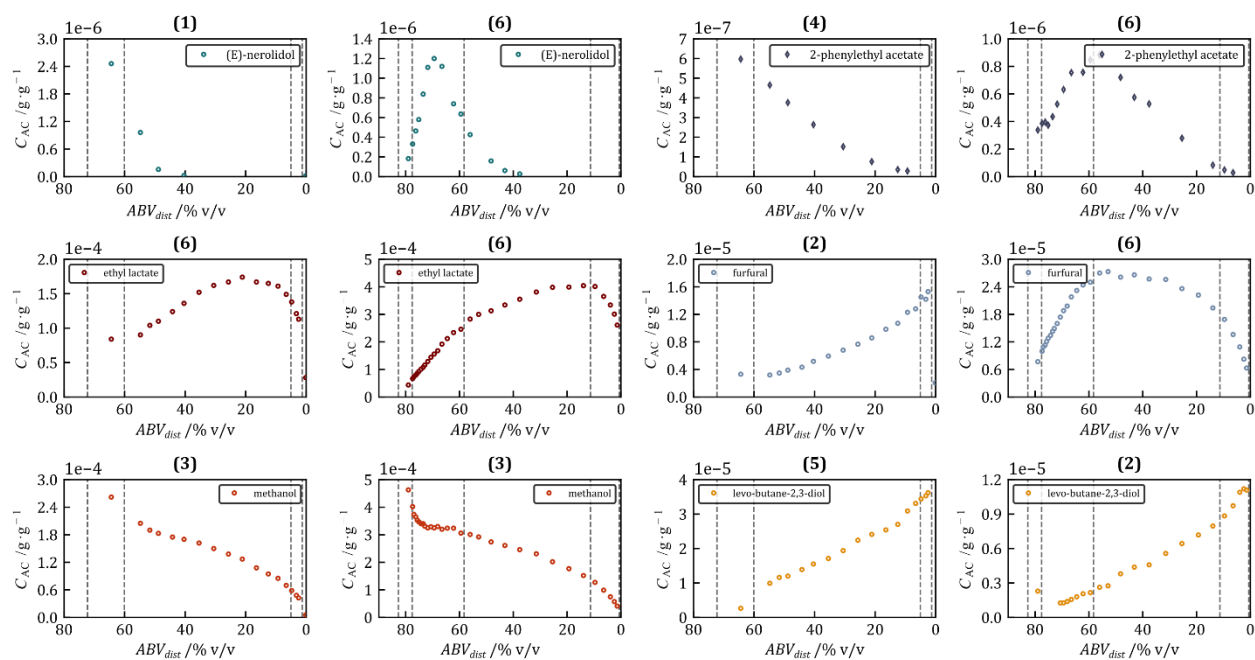


Figure 4. Concentration profiles of intermediate and heavy aroma compounds as a function of decreasing ethanol concentration (in % v/v) in the distillate during the WD and the BD. For each graph, the corresponding profile shape from Cantagrel's classification is indicated in parenthesis. Distillate cuts are represented by vertical dashed lines: H, head; B, brouillis; T, tail; Ht, heart; S, second.

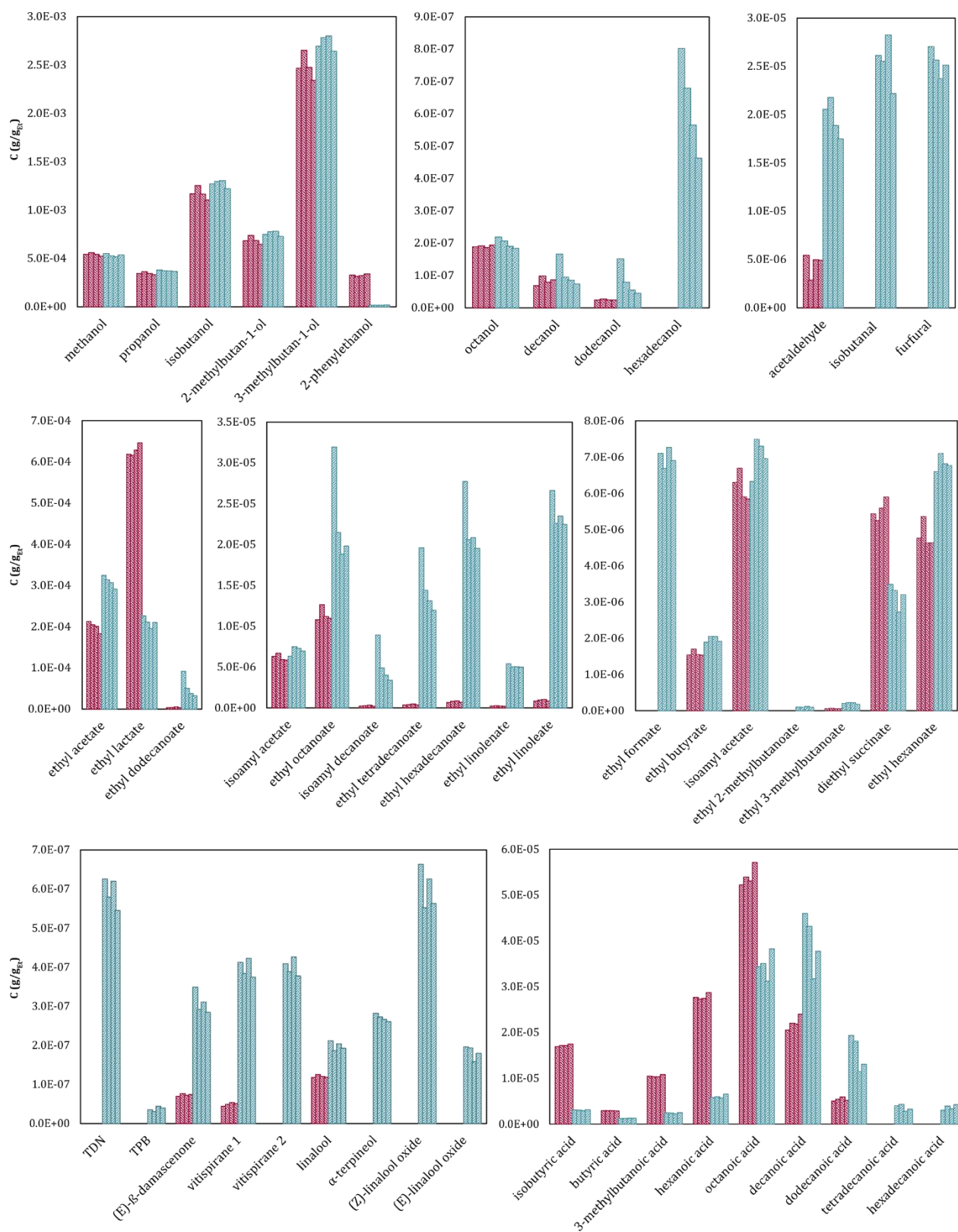


Figure 5. Changes in concentrations in relation to ethanol (g/g_{Et}) for aroma compounds in wines (■) and hearts (■) over four Charentaise distillations.

Table 1. Aroma compounds analyzed in this work with their IUPAC names, CAS numbers, analytical parameters and chemical properties^a.

Compounds	IUPAC name	CAS	Method ^b	RI ^c	LOQ ^d /g·g ⁻¹	T _b ^e /°C	M /g·mol ⁻¹	log P ^f
Alcohols								
methanol	methanol	67-56-1	A	901	6.3E-06	64.7	32.042	-0.74
allyl alcohol	prop-2-en-1-ol	107-18-6	A		1.1E-06	97.0	58.08	0.17
propanol	propan-1-ol	71-23-8	A	1029	1.1E-06	97.0	60.10	0.25
butan-2-ol	butan-2-ol	78-92-2	A		5.3E-07	98.0	74.12	0.65
isobutanol	2-methylpropan-1-ol	78-83-1	A	1076	1.1E-06	108.0	74.12	0.76
butan-1-ol	butan-1-ol	71-36-3	A	1152	1.1E-06	117.0	74.12	0.84
2-methylbutan-1-ol (active amyl alcohol)	2-methylbutan-1-ol	137-32-6	A	1209	1.1E-06	130.0	88.15	1.29
3-methylbutan-1-ol (isoamyl alcohol)	3-methylbutan-1-ol	123-51-3	A	1211	1.1E-06	130.0	88.15	1.28
(Z)-3-hexenol	(Z)-hex-3-en-1-ol	928-96-1	B, A	1371	1.1E-06	156.5	100.16	1.7
(E)-3-hexenol	(E)-hex-3-en-1-ol	928-97-2	B	1355	1.2E-07	166.0	100.16	1.61
(Z)-2-hexenol	(Z)-hex-2-en-1-ol	928-94-9	B		1.2E-07	166.0	100.16	1.76
(E)-2-hexenol	(E)-hex-2-en-1-ol	928-95-0	A		1.2E-07	159.0	100.16	1.66
hexanol	hexan-1-ol	111-27-3	B, A	1356	7.3E-08	157.1	102.18	2.03
heptan-2-ol	heptan-2-ol	543-49-7	B		3.5E-08	161.0	116.20	2.31
benzyl alcohol	phenylmethanol	100-51-6	A		5.3E-07	204.0	108.14	1.05
2-phenylethanol	2-phenylethanol	60-12-8	B, A	1921	2.2E-07	220.0	122.17	1.51
1-octen-3-ol	oct-1-en-3-ol	3391-86-4	B	1443	2.5E-08	84.5	128.22	2.52
2-ethylhexanol	2-ethylhexan-1-ol	104-76-7	B		1.9E-08	184.5	130.23	2.82
octanol	octan-1-ol	111-87-5	B	1547	2.5E-08	196.0	130.23	3.07
nonan-2-ol	nonan-2-ol	628-99-9	B	1509	1.9E-08	193.5	144.26	3.23
decanol	decan-1-ol	112-30-1	B	1752	9.5E-09	239.0	158.29	4.57
dodecanol	dodecan-1-ol	112-53-8	B	1957	9.5E-09	261.0	186.34	5.13
tetradecanol	tetradecan-1-ol	112-72-1	B	2145	9.5E-09	304.0	214.39	6.03
farnesol	(2E,6E)-3,7,11-trimethyldodeca-2,6,10-trien-1-ol	4602-84-0	B	2350	9.5E-09	149.0	222.37	4.83
hexadecanol	hexadecan-1-ol	36653-82-4	B	2400	9.5E-09	180.0	242.45	6.95
levo-butane-2,3-diol	(2R,3R)-butane-2,3-diol	6982-25-8	A		1.1E-06	77.0	90.12	0.88

Compounds	IUPAC name	CAS	Method ^b	RI ^c	LOQ ^d /g·g ⁻¹	T _b ^e /°C	M /g·mol ⁻¹	log P ^f
meso-butane-2,3-diol	(2R,3S)-butane-2,3-diol	5341-95-7	A		1.1E-06	77.3	90.12	-0.66
Esters								
ethyl formate	ethyl methanoate	109-94-4	A	811		53.0	74.08	0.23
ethyl acetate	ethyl ethanoate	141-78-6	A	<900	1.1E-06	77.0	88.11	0.73
ethyl lactate	ethyl 2-hydroxypropanoate	97-64-3	A	1331	2.1E-06	154.0	118.13	0.44
isobutyl acetate	2-methylpropyl acetate	110-19-0	A	985	5.3E-07	116.0	116.16	1.78
ethyl butyrate	ethyl butyrate	105-54-4	B, A	1022	6.3E-08	120.0	116.16	1.82
isoamyl acetate	3-methylbutyl acetate	123-92-2	B, A	1113	1.6E-08	142.0	130.19	2.03
ethyl 2-methylbutanoate	ethyl 2-methylbutanoate	7452-79-1	B	1035	2.2E-08	133.0	130.19	2.26
ethyl 3-methylbutanoate (ethyl isovalerate)	ethyl 3-methylbutanoate	108-64-5	B	1051	2.2E-08	132.0	130.19	2.26
ethyl pentanoate (ethyl valerate)	ethyl pentanoate	539-82-2	B		1.3E-08	144.5	130.19	2.31
ethyl furoate	ethyl furan-2-carboxylate	614-99-3	B		6.3E-08	196.0	140.14	1.52
(Z)-3-hexenyl acetate	[(Z)-hex-3-enyl] acetate	3681-71-8	B	1304	1.6E-08	75.5	142.20	2.42
diethyl succinate	diethyl butanedioate	123-25-1	B, A	1667	7.3E-08	218.0	174.20	1.19
ethyl hexanoate (ethyl caproate)	ethyl hexanoate	123-66-0	B, A	1223	1.3E-08	168.0	144.21	2.82
hexyl acetate	hexyl ethanoate	142-92-7	B	1263	1.3E-08	169.0	144.21	2.83
methyl salicylate	methyl 2-hydroxybenzoate	119-36-8	B	1756	1.3E-08	222.0	152.15	2.55
2-phenylethyl acetate	2-phenylethyl acetate	103-45-7	B	1805	6.3E-09	238.5	164.20	2.35
2-phenylethyl octanoate	2-phenylethyl octanoate	5457-70-5	B		9.5E-09	295.5	248.37	5.36
ethyl octanoate (ethyl caprylate)	ethyl octanoate	106-32-1	B, A	1424	1.3E-08	207.0	172.27	3.84
isobutyl decanoate	2-methylpropyl decanoate	105-79-3	B		1.6E-08	267.0	172.26	3.69
ethyl dihydrocinnamate	ethyl 3-phenylpropanoate	2021-28-5	B		9.5E-09	247.0	178.23	2.73
ethyl 9-decenoate	ethyl dec-9-enoate	67233-91-4	B	1685	9.5E-09	250.2	198.3	4.39
ethyl decanoate (ethyl caprate)	ethyl decanoate	110-38-3	B, A	1629	6.9E-08	245.0	200.32	4.79
isoamyl octanoate	3-methylbutyl octanoate	2035-99-6	B	1651	6.6E-08	260.0	214.35	5.21
ethyl dodecanoate (ethyl laurate)	ethyl dodecanoate	106-33-2	B, A	1835	9.5E-09	269.0	228.38	5.78

Compounds	IUPAC name	CAS	Method ^b	RI ^c	LOQ ^d /g·g ⁻¹	T _b ^e /°C	M /g·mol ⁻¹	log P ^f
isoamyl decanoate	3-methylbutyl decanoate	2306-91-4	B	1863	9.5E-09	286.0	242.4	6.23
ethyl tetradecanoate (ethyl myristate)	ethyl tetradecanoate	124-06-1	B	2040	9.5E-09	179.0	256.43	6.9
farnesyl acetate	[(2 <i>E</i> ,6 <i>E</i>)-3,7,11-trimethyldodeca-2,6,10-trienyl] acetate	4128-17-0	B		9.5E-09	120.0	264.41	6.14
isoamyl dodecanoate <small>(isoamyl laurate)</small>	3-methylbutyl dodecanoate	6309-51-9	B	2059	9.5E-09	190.0	270.46	7.25
ethyl hexadecanoate <small>(ethyl palmitate)</small>	ethyl hexadecanoate	628-97-7	B	2246	9.5E-09	192.5	284.48	7.92
ethyl linolenate	ethyl (9 <i>Z</i> ,12 <i>Z</i> ,15 <i>Z</i>)-octadeca-9,12,15-trienoate	1191-41-9	B	2545	9.5E-09	167.0	306.49	7.49
ethyl linoleate	ethyl (9 <i>Z</i> ,12 <i>Z</i>)-octadeca-9,12-dienoate	544-35-4	B	2515	1.3E-08	224.0	308.5	8.17
ethyl oleate	ethyl (<i>Z</i>)-octadec-9-enoate	111-62-6	B	2469	9.5E-09	217.0	310.52	8.69
ethyl octadecanoate (ethyl stearate)	ethyl octadecanoate	111-61-5	B	2455	1.3E-08	214.0	312.54	8.94
Aldehydes								
acetaldehyde <small>(ethanal)</small>	acetaldehyde	75-07-7	A	<900	1.1E-06	20.1	44.053	0.45
isobutanal	2-methylpropanal	78-84-2	A	<900	5.3E-07	63.0	72.11	0.74
furfural	furan-2-carbaldehyde	98-01-1	A		1.1E-06	162.0	96.09	0.83
benzaldehyde	benzaldehyde	100-52-7	B	1502	4.1E-08	178.5	106.12	1.48
Norisoprenoids								
TDN	1,1,6-Trimethyl-1,2-dihydronaphthalene	30364-38-6	B, A	1722	9.5E-09	242.0	172.27	4.61
TPB	(<i>E</i>)-1-(2,3,6-Trimethylphenyl)buta-1,3-diene	50686-96-9	B	1819	3.2E-09	261.0	172.27	4.62
(<i>E</i>)-β-damascenone	(<i>E</i>)-1-(2,6,6-trimethylcyclohexa-1,3-dien-1-yl)but-2-en-1-one	23726-93-4	B	1802	9.5E-09	274.0	190.29	4.40
vitispirane 1	2,6,6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene	65416-59-3	B	1531	9.5E-09	258.0	192.3	4.01
vitispirane 2	2,6,6-trimethyl-10-methylidene-1-oxaspiro[4.5]dec-8-ene	65416-59-4	B	1534	9.5E-09	258.0	192.3	4.01
Terpenes								
linalool	3,7-dimethylocta-1,6-dien-3-ol	78-70-6	B	1549	1.9E-08	195.5	154.25	3.29
α-terpineol	2-(4-methylcyclohex-3-en-1-yl)propan-2-ol	98-55-5	B	1681	1.6E-08	218.0	154.25	2.98
(<i>Z</i>)-linalool oxide	2-(5-ethenyl-5-methyloxolan-2-yl)propan-2-ol	60047-17-8	B		3.5E-08	193.0	170.25	2.43
(<i>E</i>)-linalool oxide	2-[(2 <i>S</i> ,5 <i>S</i>)-5-ethenyl-5-methyloxolan-2-yl]propan-2-ol	34995-77-2	B		4.4E-08	193.0	170.25	2.08
(<i>E</i>)-nerolidol	(6 <i>E</i>)-3,7,11-trimethyldodeca-1,6,10-trien-3-ol	40716-66-3	B	2025	9.5E-09	263.0	222.37	5.32
Acetals								

Compounds	IUPAC name	CAS	Method ^b	RI ^c	LOQ ^d /g·g ⁻¹	T _b ^e /°C	M /g·mol ⁻¹	log P ^f
diethoxy methane	ethoxymethoxyethane	462-95-3	A		5.3E-07	87.5	104.15	0.84
1,1-diethoxyethane	1,1-diethoxyethane	105-57-7	A	<900	1.1E-06	102.0	118.18	0.84
1,1,3-triethoxypropane	1,1,3-triethoxypropane	7789-92-6	B, A	1297	5.3E-07	185.0	176.26	1.61
1,1-diethoxyisobutane	1,1-diethoxy-2-methylpropane	1741-41-9	B	975	2.2E-08	136.0	146.2	1.89
Acids								
acetic acid	acetic acid	64-19-7	C	1445	2.0E-05	117.5	60.052	-0.17
propanoic acid	propanoic acid	79-09-4	C	1528	1.2E-06	141.0	74.08	0.33
2-methylpropanoic acid (isobutyric acid)	2-methylpropanoic acid	79-31-2	C	1556	1.2E-06	153.5	88.11	0.94
butyric acid	butanoic acid	107-92-6	C	1620	2.0E-06	162.0	88.11	0.79
3-methylbutanoic acid (isovaleric acid)	3-methylbutanoic acid	503-74-2	C	1660	1.2E-06	176.0	102.13	1.16
pentanoic acid (valeric acid)	pentanoic acid	109-52-4	C		1.2E-06	110.5	102.13	1.39
hexanoic acid (caproic acid)	hexanoic acid	142-62-1	C	1840	1.2E-06	202.5	116.16	1.92
octanoic acid (caprylic acid)	octanoic acid	124-07-2	C	2051	1.2E-06	237.0	144.21	3.05
decanoic acid (capric acid)	decanoic acid	334-48-5	C	2264	1.2E-06	268.7	172.27	4.09
dodecanoic acid (lauric acid)	dodecanoic acid	143-07-7	C	2469	1.2E-06	225.0	200.32	4.6
tetradecanoic acid (myristic acid)	tetradecanoic acid	544-63-8	C	2550	1.2E-06	250.0	228.38	6.11
palmitoleic acid	(Z)-hexadec-9-enoic acid	373-49-9	C		2.0E-06	364.0	254.41	6.4
hexadecanoic acid (palmitic acid)	hexadecanoic acid	57-10-3	C		1.2E-06	271.5	256.43	7.17
linolenic acid	(9Z,12Z,15Z)-octadeca-9,12,15-trienoic acid	463-40-1	C		2.0E-06	443.0	278.44	6.46
linoleic acid	(9Z,12Z)-octadeca-9,12-dienoic acid	60-33-3	C		2.0E-06	229.5	280.45	7.05
oleic acid	(Z)-octadec-9-enoic acid	112-80-1	C		2.0E-06	194.5	282.47	7.7
octadecanoic acid (stearic acid)	octadecanoic acid	57-11-4	C		2.0E-06	361.0	284.48	8.23
Other								

Compounds	IUPAC name	CAS	Method ^b	RI ^c	LOQ ^d /g·g ⁻¹	T _b ^e /°C	M /g·mol ⁻¹	log P ^f
(Z)-whiskey lactone	(4R,5R)-5-butyl-4-methyloxolan-2-one	55013-32-6	B		1.9E-08			
(E)-whiskey lactone	(4S,5R)-5-butyl-4-methyloxolan-2-one	80041-01-6	B		1.6E-08			
acrolein	prop-2-enal	107-02-8	A		5.3E-07	53.0	56.064	-0.01
acetoin	3-hydroxybutan-2-one	513-86-0	A		1.1E-06	148.0	88.11	-0.36

^aCompounds in italics were not detected in the samples or were below their limits of detection; for compounds with more than one commonly used name in the literature, the alternative name is indicated in parenthesis. ^bA= direct injection; B = isooctane extraction; C = fatty acids extraction. ^cRetention indexes in a polar (WAX) column. ^dLimit of quantitation. ^eT_b, boiling temperature at 101.3 kPa; M, molar mass. ^foctanol-water partition coefficients from Li et al. (1998); Piombino et al. (2019); Villamor & Ross (2013); Wang et al. (2019), The Good Scents Company database (<http://www.thegoodscentscompany.com/index.html>), Haynes (2017).

Table 2. Masses and ethanol concentration of the boiler loads and of the resulting distillate fractions and residue during the wine and brouillis distillations.

	m /kg	m_{Et} /kg	ABV ¹ /% v/v	x_{Et} /g·g ⁻¹
Wine distillation				
Load	2385.0	175.9	9.2	0.074
Out				
Head	4.3	2.4	64.4	0.565
Brouillis	656.4	168.7	31.3	0.257
Tail	107.6	3.0	3.5	0.028
Residue	1617.9	1.8	0.1	0.001
Brouillis distillation				
Load	2398.2	618.4	31.4	0.258
Out				
Head	17.9	13.0	79.0	0.723
Heart	729.1	464.9	71.3	0.638
Second	433.6	130.7	36.4	0.302
Tail	271.2	8.9	4.1	0.033
Residue	947.2	0.9	0.1	0.001

¹ABV = alcohol by volume, which expresses ethanol concentration in % v/v at 20 °C.

Table 3. Proposed classification of aroma compounds according to their volatilities in the boiling liquid, their concentration profiles based on Cantagrel (1989) and their chemical properties.

	Volatility at $0 < x_{Et} < 0.26$ /g·g ⁻¹				Cantagrel classification		Chemical properties		
	K_{max}	K_{min}	$(\alpha_{AC/Et})_{max}$	$(\alpha_{AC/Et})_{min}$	WD	BD	$\log P$	T_b /°C	M /g·mol ⁻¹
Light									
L-I	34 - 1000	>16	3 - 83	>3.8	1	1	0.2 - 3.8	20 - 240	44 - 200
L-II	100	>6	8.2	>1.4	1	1,8	3.3 - 5.2	195 - 267	154 - 214
L-III	-	-	-	-	1	7,3	1.9 - 8	85 - 305	128 - 284
L-IV	16 - 35	>4.5	1.4 - 2.9	>0.8	4	7	0.2 - 2	97 - 157	60 - 102
Intermediate									
I-I	6	>3	0.6	>0.7	3	3	-0.7	65	32
I-II	65	>2.3	5.4	>0.5	1	6	4.4 - 8.9	120 - 296	190 - 264
I-III	18 - 34	>1.5	1.5 - 2.8	>0.3	4	6	1.5 - 3	156 - 238	100 - 164
I-IV	1.3 - 17	>0.2	0.2 - 1.4	>0.03	2,5,6	6	0.4 - 4.6	141 - 268	74 - 200
Heavy									
H-I	0.7 - 1	>0.2	0.06 - 1	>0.06	2	2	-0.9 - 0.3	77 - 148	60 - 90

K and $\alpha_{AC/Et}$, absolute volatility and relative volatility in relation to ethanol in pure water (max) and at 0.26 g·g⁻¹ ethanol concentration in the boiling liquid (min); $\log P$, octanol/water partition coefficient; T_b , boiling temperature at 101.3 kPa; M , molecular weight.

Table 4. List of aroma compounds in each group according to the proposed classification system^{1,2}.

Compounds by group	
Light	L-I isoamyl acetate, ethyl 3-methylbutanoate, ethyl acetate, ethyl hexanoate, ethyl octanoate, ethyl decanoate, ethyl formate*, isobutyl acetate*, ethyl butyrate*, ethyl 2-methylbutanoate*, hexyl acetate*, ethyl propanoate ⁺ , ethyl 2-methylpropanoate [#] , 3-methylbutan-1-al [#] , butanal [#] , pentanal [#] , propanal [#] , isobutanal, acetaldehyde, 1,1-diethoxyethane.
	L-II isoamyl octanoate*, isobutyl decanoate*, isoamyl tetradecanoate*, TDN*, vitispirane 1*, vitispirane 2*, TPB*, (<i>Z</i>)-linalool oxide, linalool.
	L-III hexadecanol*, 1-octen-3-ol*, 2-ethylhexanol*, octanol*, nonan-2-ol*, decanol*, dodecanol*, tetradecanol*, 2-methylpropan-2-ol [#] , propan-2-ol [#] , propen-2-ol [#] , ethyl dodecanoate*, ethyl tetradecanoate*, ethyl hexadecanoate*, isoamyl decanoate*, isoamyl dodecanoate*, 1,1-diethoxyisobutane*.
	L-IV propanol, isobutanol, butan-1-ol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, hexanol.
Intermediate	I-I methanol.
	I-II farnesol*, farnesyl acetate*, ethyl octadecanoate*, ethyl oleate*, ethyl linoleate ⁺ , ethyl linolenate ⁺ , (<i>E</i>)-nerolidol*, (<i>E</i>)- β -damascenone.
	I-III (<i>Z</i>)-3-hexenol, 2-phenylethyl acetate, ethyl furoate*, α -terpineol.
	I-IV 2-phenylethanol, ethyl lactate, diethyl succinate, methyl salicylate*, furfural, (<i>E</i>)-linalool oxide*, butyric acid, 3-methylbutanoic acid, 2-methylpropanoic acid, hexanoic acid, octanoic acid, decanoic acid*, 2-methylbutanoic acid [#] .
Heavy	H-I levo-butane-2,3-diol*, meso-butane-2,3-diol*, acetic acid, propanoic acid, formic acid [#] .

¹Compounds marked with an asterisk (*) were classified according to their plotted concentration profiles (in the absence of VLE data), whereas those marked with a plus sign (+) were classified based on their profiles proposed by Cantagrel (1989) and those with a hashtag (#) were grouped according to their volatilities from Puentes et al. (2018a).

Table 5. Distribution of volatile aroma compounds between distillate fractions, their classification between light (L), intermediate (I) and heavy (H) subgroups and their quantitative changes throughout the charentaise distillation^{a,b}.

	Class	Wine distillation				Brouillis distillation					Wine distillation			Brouillis distillation		
		H%	B%	T%	R%	H%	Ht%	S%	T%	R%	in /g	Σ out /g	out/in	in /g	Σ out /g	out/in
ethanol		1.4	95.9	1.7	1.0	2.1	75.2	21.1	1.4	0.1	175899.0	175870.6	1.00	618360.4	618287.3	1.00
Alcohols																
methanol	I-I	1.1	85.9	4.9	8.1	2.2	65.2	26.9	5.7	0.0	103.643	106.953	1.03	356.478	379.769	1.07
propanol	L-IV	2.1	96.5	0.6	0.8	2.2	81.8	14.7	0.5	0.8	62.349	62.272	1.00	198.776	212.791	1.07
isobutanol	L-IV	4.1	95.5	0.0	0.4	3.2	92.0	4.8	0.0	0.0	215.235	206.229	0.96	619.324	649.434	1.05
butan-1-ol	L-IV	100.0	0.0	0.0	0.0	2.1	97.9	0.0	0.0	0.0	<LOQ	0.016	-	<LOQ	1.545	+++
2-methylbutan-1-ol	L-IV	4.7	94.9	0.0	0.4	2.5	93.1	4.4	0.0	0.0	125.629	118.434	0.94	360.598	382.658	1.06
3-methylbutan-1-ol	L-IV	4.0	95.6	0.0	0.4	2.1	91.2	6.6	0.0	0.2	449.714	430.162	0.96	1324.515	1406.739	1.06
(Z)-3-hexenol	I-III	2.2	97.8	0.0	0.0	1.0	70.4	28.2	0.3	0.0	0.649	0.626	0.97	2.307	2.443	1.06
(E)-3-hexenol						14.7	0.0	85.3	0.0	0.0	<LOQ	0.000	-	0.000	0.026	-
hexanol	L-IV	4.3	95.7	0.0	0.0	1.4	90.5	6.7	1.4	0.0	2.723	2.627	0.96	8.115	8.374	1.03
2-phenylethanol	I-IV	0.2	39.6	9.2	51.0	0.1	8.5	25.4	25.6	40.4	62.173	57.253	0.92	93.733	98.032	1.05
1-octen-3-ol	L-III					5.7	94.3	0.0	0.0	0.0	<LOQ	0.001	-	0.000	0.021	-
2-ethylhexanol	L-III					6.1	88.2	0.0	5.7	0.0	<LOQ	0.001	-	<LOQ	0.021	-
octanol	L-III	9.0	91.0	0.0	0.0	2.7	92.4	4.9	0.0	0.0	0.033	0.029	0.87	0.092	0.102	1.10
nonan-2-ol	L-III					3.5	96.5	0.0	0.0	0.0	<LOQ	0.001	-	0.000	0.019	-
decanol	L-III	13.8	86.2	0.0	0.0	3.2	92.7	2.9	1.3	0.0	0.016	0.013	0.79	0.045	0.047	1.05
dodecanol	L-III	7.2	92.8	0.0	0.0	5.4	91.7	0.0	2.9	0.0	0.006	0.011	1.91	0.037	0.041	1.11
tetradecanol	L-III	4.7	79.4	2.4	13.4	1.3	85.2	9.5	1.3	2.7	0.035	0.114	3.20	0.504	0.603	1.19
farnesol	I-II	2.8	65.3	0.0	32.0	2.5	68.9	25.7	2.8	0.0	0.055	0.025	0.46	0.115	0.071	0.62
hexadecanol	L-III	5.8	91.4	2.8	0.0	3.1	78.7	6.8	1.1	10.4	<LOQ	0.081	+++	0.237	0.368	1.55
Esters																
ethyl formate	L-I	4.7	95.3	0.0	0.0	19.3	64.3	16.4	0.0	0.0	0.000	0.953	+++	1.823	4.278	2.35
ethyl acetate	L-I	18.3	80.0	0.6	1.0	18.2	80.1	1.4	0.3	0.0	48.590	45.184	0.93	162.172	158.804	0.98
ethyl lactate	I-IV	0.2	60.6	8.9	30.3	0.2	24.7	37.4	22.8	14.9	129.996	150.033	1.15	426.016	400.278	0.94
ethyl butyrate	L-I	54.5	45.5	0.0	0.0	23.0	75.8	1.2	0.0	0.0	0.350	0.248	0.71	1.111	1.033	0.93
isoamyl acetate	L-I	64.7	35.3	0.0	0.0	20.8	79.1	0.0	0.0	0.0	1.334	0.916	0.69	3.436	3.505	1.02
ethyl 2-methylbutanoate	L-I	100.0	0.0	0.0	0.0	23.1	69.2	7.8	0.0	0.0	0.010	0.005	0.53	<LOQ	0.053	-

		Wine distillation				Brouillis distillation					Wine distillation			Brouillis distillation		
	Class	H%	B%	T%	R%	H%	Ht%	S%	T%	R%	in /g	Σ out /g	out/in	in /g	Σ out /g	out/in
ethyl 3-methylbutanoate	L-I	100.0	0.0	0.0	0.0	17.8	74.7	7.5	0.0	0.0	0.016	0.011	0.65	0.097	0.103	1.06
ethyl furoate	I-III	1.4	98.6	0.0	0.0	1.2	62.0	35.5	1.3	0.0	<LOQ	0.080	-	0.362	0.372	1.03
(Z)-3-hexenyl acetate						5.7	94.3	0.0	0.0	0.0	<LOQ	0.000	-	<LOQ	0.027	-
diethyl succinate	I-IV	0.5	78.1	7.9	13.5	0.2	21.6	53.9	18.2	6.1	1.172	1.105	0.94	6.307	6.861	1.09
ethyl hexanoate	L-I	68.8	30.4	0.0	0.8	17.8	78.7	3.3	0.3	0.0	1.193	0.793	0.66	3.331	3.362	1.01
hexyl acetate	L-I	67.0	33.0	0.0	0.0	15.4	84.6	0.0	0.0	0.0	0.053	0.035	0.66	0.117	0.135	1.15
methyl salicylate	I-IV	0.0	87.3	12.7	0.0	0.0	85.0	15.0	0.0	0.0	0.004	0.009	2.26	0.027	0.027	0.99
2-phenylethyl acetate	I-III	2.0	98.0	0.0	0.0	1.0	62.6	35.5	0.9	0.0	0.110	0.126	1.15	0.547	0.622	1.14
2-phenylethyl octanoate	I-II	3.7	96.3	0.0	0.0	1.0	72.2	24.1	2.7	0.0	0.009	0.017	1.92	0.077	0.128	1.66
ethyl octanoate	L-I	77.3	22.0	0.1	0.5	12.6	82.5	4.6	0.2	0.0	2.866	2.369	0.83	16.719	10.192	0.61
isobutyl decanoate	L-II	39.5	54.1	0.0	6.4	12.2	85.2	2.0	0.5	0.0	0.020	0.062	3.17	0.297	0.269	0.91
ethyl 9-decenoate						3.2	63.9	27.6	5.3	0.0	<LOQ	0.000	-	0.030	0.036	1.21
ethyl decanoate	L-I	53.1	34.8	5.6	6.6	7.4	69.4	2.7	1.5	18.9	5.006	6.312	1.26	45.393	23.661	0.52
isoamyl octanoate	L-II	100.0	0.0	0.0	0.0	14.3	85.7	0.0	0.0	0.0	0.071	0.080	1.13	0.559	0.457	0.82
ethyl dodecanoate	L-III	31.3	61.0	0.1	7.6	7.1	91.8	0.6	0.0	0.5	1.429	3.975	2.78	36.814	21.740	0.59
isoamyl decanoate	L-III	21.8	73.1	0.0	5.1	9.7	90.1	0.2	0.0	0.0	0.107	0.496	4.63	2.325	2.072	0.89
ethyl tetradecanoate	L-III	6.2	88.4	1.0	4.5	5.5	92.9	0.8	0.1	0.8	0.165	1.438	8.70	9.276	6.486	0.70
farnesyl acetate	I-II	7.1	74.8	0.0	18.1	0.7	91.1	8.2	0.0	0.0	0.028	0.043	1.56	0.107	0.211	1.97
isoamyl dodecanoate	L-III	4.6	89.6	2.0	3.8	8.1	91.6	0.3	0.0	0.0	0.020	0.240	12.20	1.503	0.911	0.61
ethyl hexadecanoate	L-III	3.5	86.8	3.8	5.9	6.7	89.9	1.0	0.2	2.2	0.279	2.180	7.80	9.633	9.930	1.03
ethyl linolenate	I-II	7.6	86.1	2.6	3.8	5.1	81.1	10.2	0.6	2.9	0.197	0.827	4.20	1.568	2.844	1.81
ethyl linoleate	I-II	6.9	84.9	3.6	4.7	6.4	83.4	4.9	0.7	4.7	0.742	3.256	4.39	7.159	12.286	1.72
ethyl oleate	I-II	6.3	84.7	4.3	4.7	7.3	82.6	2.6	0.5	6.9	0.090	0.387	4.28	0.976	1.671	1.71
ethyl octadecanoate	L-III	7.7	79.3	5.0	7.9	7.4	79.9	0.9	0.6	11.2	0.050	0.135	2.68	0.370	0.714	1.93
Aldehydes																
acetaldehyde	L-I	2.1	54.2	7.4	36.3	9.4	55.5	4.8	4.6	25.7	1.146	5.484	4.79	11.086	12.735	1.15
isobutanal	L-I	7.8	74.9	17.3	0.0	31.3	67.3	0.0	1.5	0.0	1.087	5.886	5.41	13.408	12.653	0.94
furfural	I-IV	0.1	48.4	16.5	34.9	0.5	47.0	40.8	11.6	0.0	1.442	9.533	6.61	24.919	25.684	1.03
benzaldehyde	I-IV	2.8	28.8	0.0	68.5	1.9	49.2	21.1	3.6	24.2	0.054	0.176	3.25	0.200	0.351	1.76

Norisoprenoids

	Class	Wine distillation				Brouillis distillation					Wine distillation			Brouillis distillation		
		H%	B%	T%	R%	H%	Ht%	S%	T%	R%	in /g	Σ out /g	out/in	in /g	Σ out /g	out/in
TDN	L-II	16.8	76.4	3.9	2.8	18.9	76.5	3.7	0.8	0.0	0.024	0.091	3.81	0.205	0.270	1.32
TPB	L-II	7.4	92.6	0.0	0.0	7.1	77.6	9.7	5.5	0.0	<LOQ	0.005	-	0.010	0.023	2.34
(<i>E</i>)-β-damascenone	I-II	2.6	91.6	5.8	0.0	1.2	91.2	7.6	0.0	0.0	0.017	0.047	2.82	0.125	0.162	1.30
vitispirane 1	L-II	7.2	92.8	0.0	0.0	11.4	76.2	10.8	1.7	0.0	0.017	0.071	4.20	0.195	0.207	1.06
vitispirane 2	L-II	9.5	90.5	0.0	0.0	15.1	82.0	2.5	0.4	0.0	0.009	0.066	7.36	0.157	0.184	1.17
Terpenes																
linalool	L-II	7.6	92.4	0.0	0.0	14.9	80.4	4.1	0.6	0.0	0.024	0.041	1.70	0.092	0.122	1.32
α-terpineol	I-III	0.6	99.4	0.0	0.0	2.9	68.4	27.4	1.3	0.0	0.012	0.043	3.51	0.165	0.179	1.09
(<i>Z</i>)-linalool oxide	L-II	25.4	69.2	5.4	0.0	26.7	53.4	18.5	1.5	0.0	0.034	0.124	3.67	0.195	0.389	2.00
(<i>E</i>)-linalool oxide	I-IV					1.0	51.2	44.9	2.8	0.0				0.142	0.179	1.26
(<i>E</i>)-nerolidol	I-II	9.5	63.6	0.0	26.9	0.5	92.5	7.0	0.0	0.0	0.102	0.112	1.10	0.350	0.619	1.77
Acetals																
1,1-diethoxyethane	L-I	3.3	40.3	0.0	56.4	19.6	73.1	0.0	7.3	0.0	0.679	2.204	3.24	5.668	3.031	0.53
1,1-diethoxyisobutane	L-III	9.3	76.6	8.8	5.2	41.4	56.6	1.7	0.2	0.0	0.592	1.176	1.99	3.743	1.991	0.53
Other																
acetoin	H-I	0.1	32.7	7.6	59.7	0.0	11.6	20.9	19.2	48.3	14.359	12.132	0.84	14.207	14.895	1.05

^aIn/out ratios correspond to the sum of the masses of a compound in the distillate fractions and in the residue divided by their mass in the boiler load ; In/out ratios higher than 1.5 are in bold, whereas those lower than 0.66 are in gray; compounds present in the distillate but not quantified in the wine are denoted by +++. ^bH = head; B = brouillis; T = tail; R = residue; Ht = heart; S = second.

Table 6. List of odorant compounds with respective odor thresholds (OT) and odor activity values (OAV) in the hearts.

Compounds	Aroma quality ^a	OT ^b ($\mu\text{g}\cdot\text{L}^{-1}$)	Source	OT ^c ($\text{g}\cdot\text{g}^{-1}$)	C _{hearts} ^d ($\text{g}\cdot\text{g}^{-1}$)	C _{hearts_40% v/v} ^e ($\text{g}\cdot\text{g}^{-1}$)	OAV ^f
Alcohols							
methanol	alcoholic	20000	a	2.11E-05	3.4E-04	1.9E-04	9.12
propanol	alcoholic, fermented	40000	a	4.22E-05	2.3E-04	1.3E-04	3.18
isobutanol	malty, alcoholic	28300	h	2.99E-05	8.1E-04	4.6E-04	15.41
butan-1-ol	malty, alcoholic	2730	h	2.88E-06	2.0E-06	1.1E-06	0.40
2-methylbutan-1-ol	alcoholic, fatty	211800	d	2.23E-04	4.8E-04	2.7E-04	1.23
3-methylbutan-1-ol	malty, cocoa	56100	b	5.92E-05	1.7E-03	9.9E-04	16.67
(Z)-3-hexenol	green, herb	1257	d	1.33E-06	2.3E-06	1.3E-06	0.98
hexanol	green, herb	8000	d	8.44E-06	1.0E-05	5.9E-06	0.70
2-phenylethanol	floral, honey	2600	b	2.74E-06	1.1E-05	6.2E-06	2.27
1-octen-3-ol	earthy, mushroom	6.12	h	6.46E-09	2.8E-08	1.6E-08	2.46
2-ethylhexanol	citrus, oily				3.1E-08	1.8E-08	-
octanol	waxy, green, orange	1100	i	1.16E-06	1.3E-07	7.2E-08	0.06
nonan-2-ol	waxy, green, creamy				2.5E-08	1.4E-08	-
decanol	fatty, floral, orange	210	m	2.22E-07	6.7E-08	3.8E-08	0.17
dodecanol	waxy, soapy, earthy	1000	m	1.05E-06	5.2E-08	3.0E-08	0.03
tetradecanol	waxy, coconut	5000	m	5.27E-06	7.2E-07	4.1E-07	0.08
farnesol	floral, sweet				8.6E-08	4.9E-08	-
hexadecanol	waxy, clean, cloth	1100	m	1.16E-06	4.0E-07	2.3E-07	0.20
levo-butane-2,3-diol	green				1.2E-06	6.9E-07	-
Esters							
ethyl formate	green, alcohol				4.4E-06	2.5E-06	-
ethyl acetate	fruity, nail polish	4000	a	4.22E-06	2.0E-04	1.1E-04	26.49
ethyl lactate	fruity	10000	a	1.05E-05	1.3E-04	7.6E-05	7.21
isobutyl acetate	floral, fruity, banana	922	h	9.73E-07	5.8E-07	3.3E-07	0.34
ethyl butyrate	apple, aniseed	9	b	9.49E-09	1.2E-06	7.1E-07	75.23
isoamyl acetate	fruity, banana, pear	245	b	2.58E-07	4.4E-06	2.5E-06	9.81
ethyl 2-methylbutanoate	fruity, apple	0.22	d	2.32E-10	6.4E-08	3.6E-08	156.86

Compounds	Aroma quality ^a	OT ^b ($\mu\text{g}\cdot\text{L}^{-1}$)	Source	OT ^c ($\text{g}\cdot\text{g}^{-1}$)	C _{heart} ^d ($\text{g}\cdot\text{g}^{-1}$)	C _{heart} 40% v/v ^e ($\text{g}\cdot\text{g}^{-1}$)	OAV ^f
ethyl 3-methylbutanoate	fruity, blueberry	1.6	b	1.69E-09	1.3E-07	7.3E-08	43.33
ethyl furoate	balsamic	132000	i	1.39E-04	3.2E-07	1.8E-07	0.00
(Z)-3-hexenyl acetate	green, fruity				-	-	-
diethyl succinate	sweet	2000	a	2.11E-06	2.0E-06	1.1E-06	0.54
ethyl hexanoate	fruity, pineapple	30	b	3.16E-08	4.3E-06	2.5E-06	77.89
hexyl acetate	fruity	1100	c	1.16E-06	1.8E-07	1.0E-07	0.09
methyl salicylate	sweet, minty				3.0E-08	1.7E-08	-
2-phenylethyl acetate	fruity, floral, rose	108	b	1.14E-07	5.1E-07	2.9E-07	2.58
2-phenylethyl octanoate	waxy, cocoa				1.1E-07	6.4E-08	-
ethyl octanoate	pineapple, green	147	b	1.55E-07	1.5E-05	8.3E-06	53.72
isobutyl decanoate	fruity, pineapple				4.4E-07	2.5E-07	-
ethyl 9-decenoate	fruity, fatty				2.9E-08	1.7E-08	-
ethyl decanoate	pear, floral	420	l	4.43E-07	3.6E-05	2.1E-05	47.03
isoamyl octanoate	fruity, oily, pineapple	600	m	6.33E-07	8.4E-07	4.8E-07	0.76
ethyl dodecanoate	sweet, floral	1600	a	1.69E-06	3.4E-05	1.9E-05	11.37
isoamyl decanoate	waxy, banana	5000	m	5.27E-06	3.4E-06	1.9E-06	0.36
ethyl tetradecanoate	sweet, waxy	46606	i	4.92E-05	9.4E-06	5.3E-06	0.11
farnesyl acetate	oily				3.0E-07	1.7E-07	-
isoamyl dodecanoate	waxy, fatty, wine				1.4E-06	7.9E-07	-
ethyl hexadecanoate	waxy, fruity, creamy	39299	i	4.15E-05	1.4E-05	8.0E-06	0.19
ethyl linolenate					3.2E-06	1.9E-06	-
ethyl linoleate	fatty	450	m	4.75E-07	1.5E-05	8.6E-06	18.12
ethyl oleate	fatty	870	m	9.18E-07	2.0E-06	1.2E-06	1.26
ethyl stearate	waxy	500	m	5.27E-07	8.7E-07	5.0E-07	0.94
Aldehydes							
acetaldehyde	green, pungent, sweet	19200	d	2.03E-05	1.2E-05	7.1E-06	0.35
isobutanal	green, herb	5.9	b	6.22E-09	1.6E-05	9.2E-06	1482.83
furfural	smoky, nutty	44000	h	4.64E-05	1.6E-05	9.2E-06	0.20
benzaldehyde	nutty, almond	4200	h	4.43E-06	3.2E-07	1.8E-07	0.04

Norisoprenoids							
TDN	kerosene				3.7E-07	2.1E-07	-
TPB					2.4E-08	1.4E-08	-
(<i>E</i>)- β -damascenone	fruity, cooked apple	0.14	d	1.48E-10	2.0E-07	1.1E-07	757.03
vitispirane 1	floral				2.5E-07	1.4E-07	-
vitispirane 2	floral				2.5E-07	1.4E-07	-
Terpenes							
linalool	citrus, lemon	115	f	1.21E-07	1.3E-07	7.2E-08	0.59
α -terpineol	floral, pine	1000	f	1.05E-06	1.7E-07	9.8E-08	0.09
(<i>Z</i>)-linalool oxide	floral, musty, herbal	5000	g	5.27E-06	3.8E-07	2.2E-07	0.04
(<i>E</i>)-linalool oxide	flower, wood	5000	g	5.27E-06	1.1E-07	6.6E-08	0.01
(<i>E</i>)-nerolidol	floral, green, citrus	99	k	1.04E-07	8.8E-07	5.0E-07	4.79
Acetals							
diethoxy methane					-	-	-
1,1-diethoxyethane	ethereal, green, nutty	719	b	7.58E-07	6.2E-06	3.6E-06	4.69
1,1,3-triethoxypropane		3700	j	3.90E-06	9.0E-09	5.1E-09	0.00
1,1-diethoxyisobutane					3.6E-06	2.1E-06	-
Acids							
acetic acid	vinegar	75521	d	7.97E-05	3.6E-05	2.1E-05	0.26
propanoic acid	pungent, acidic, cheesy	18100	i	1.91E-05	4.5E-07	2.6E-07	0.01
2-methylpropanoic acid	acidic, cheesy, rancid	1580	h	1.67E-06	3.0E-06	1.7E-06	1.04
butyric acid	buttery, cheese	1200	c	1.27E-06	1.2E-06	7.1E-07	0.56
3-methylbutanoic acid	cheese, sweat	78	e	8.23E-08	2.4E-06	1.4E-06	16.60
hexanoic acid	sweaty, rancid	1000	d	7.98E-06	6.0E-06	3.4E-06	0.43
octanoic acid	oily, fatty, cheese	2800	a	1.05E-06	3.5E-05	2.0E-05	18.73
decanoic acid	soapy, musty	7563	c	2.95E-06	3.9E-05	2.3E-05	7.64
dodecanoic acid	fatty, coconut	7200	m	7.59E-06	1.5E-05	8.8E-06	1.16
tetradecanoic acid	waxy, fatty, coconut	12000	m	1.27E-05	3.6E-06	2.1E-06	0.16
hexadecanoic acid	waxy, fatty	10000	m	1.05E-05	3.6E-06	2.1E-06	0.20

^aFrom The Good Scents Company database (<http://www.thegoodscentscompany.com>). ^bOdor thresholds in hydroalcoholic solutions at 40% v/v ethanol ((A)Berger et al. (2007); (B) Poisson & Schieberle (2008); (C) Willner et al. (2013); (D) Uselmann & Schieberle (2015); (E) Franitza et al. (2016a); (F) Thibaud et al. (2020); (G) Cacho et al. (2012)), 46% v/v ethanol ((H) Gao et al. (2014); (I) Sun et al. (2018); (J) Fan et al. (2015); (K) Wang et al. (2016)), 35% v/v ethanol ((L) Pino et al. 2012)) or 43% v/v

ethanol ((M) Salo et al. (1972)). ^cOdor thresholds converted to g·g⁻¹. ^dAverage concentration in the hearts (~71% v/v ethanol). ^eAverage concentration in the hearts after dilution to 40% v/v ethanol. ^fOdor Activity Value in hearts diluted to 40% v/v ethanol, with OAV>1 in bold.