# The Evolution of Volatile Compounds during the Distillation of Cognac Spirit.

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## ABSTRACT

Cognac wine spirit has a complex composition in volatile compounds which contribute to its organoleptic profile. This work focused on the batch distillation process and, in particular, on volatile compounds specifically produced by chemical reactions during the distillation of Cognac wine spirit, traditionally conducted in two steps with charentais pot stills. The aim of this study was to characterize these volatile compounds formed during distillation. Sampling has been performed on the distillates and inside the boiler during a typical Cognac distillation. The analysis of these samples allowed to perform a mass balance and to point out several types of volatile compounds whose quantities strongly increased during the distillation process. These compounds were distinguished by their chemical family. It has been found that the first distillation step was decisive for the formation of volatile compounds. Moreover, 2 esters, 3 aldehydes, norisoprenoids and terpenes were shown to be generated during the process. These results suggest that some volatile compounds found in Cognac spirit are formed during distillation due to chemical reactions and high temperature induced by the process. These findings give important indications to professional distillers in order to enhance the product's quality.

**Keywords:** Cognac spirit; pot still batch distillation; volatile compounds; chemical reactivity

## INTRODUCTION

Cognac is a prestigious French wine spirit exclusively produced in Charente, Charente Maritime and some neighboring communities (France). The "Charentaise distillation" of Cognac spirit is a traditional batch process well described in terms of equipment and operations by the distillers and the Appellation d'Origine Controlée (AOC) or "Controlled Designation of Origin" decree.[1] Moreover, Cognac spirit has a complex composition in volatile compounds which contribute to the product's typical aroma perceived by the consumer. These compounds have different origins: they come from grape musts, are formed during alcoholic fermentation, are produced during the distillation process[2] and after, by the ageing process in wooden casks.[3–6]

The volatile compounds found in distilled beverages have been reported in the literature.[5,7] The aroma compounds involved in the odor perception are sorted by chemical classes such as alcohols, esters, aldehydes, norisoprenoids and terpenes. Moreover, extensive studies on their formation during grapes' maturation and musts' fermentation have been conducted. Alcohols found in Cognac spirit are mainly formed during fermentation from amino acids that undergo a deamination and a decarboxylation by yeast's biosynthesis.[7–9] Carboxylic acids are also formed by the biosynthesis of the yeast during the fermentation step,[10] and are found to participate in the overall aroma of freshly distilled Cognac spirit.[11] Esters have a great impact on the Cognac spirit's perception and are mainly synthesized by yeast during alcoholic fermentation. Esters can also be derived from the grape, from the chemical esterification of alcohols and from acids during wine ageing.[4,12–15] Aldehydes and ketones can contribute to unpleasant green notes in wine,[16] whisky,[17] and Cognac.[18] Terpenes and norisoprenoids such as linalool, nerolidol, β-damascenone and vitispiranes have been shown to be key odorant compounds in freshly distilled Cognac spirit.[11] Terpenes and $C_{13}$-norisoprenoids are already present in vines and grape musts under two forms : free and glycosylated.[19,20] The quantity of glycosidically bound volatiles is estimated to be two to eight times greater than their free counterparts.[21] While glycosylated compounds are not contributing to aroma directly, they are considered as important aroma precursors.[22] Glycosylated compounds can be hydrolyzed by acid[22–24] or by enzymes[21,25] during fermentation. Upon hydrolysis, the aglycon is liberated in the wine, and becomes sensorially active. However, compound formation during distillation remains poorly studied and understood, making the distillation process hard to control regarding the specific volatile generated by heating during distillation. Hence, this work focuses on the "Charentaise" distillation process and, in particular, on volatile compounds specifically produced by chemical reactions during heating in a charentais pot still.

The Charentaise batch distillation method to obtain Cognac spirit is performed by using a pot still made of copper. The process is conducted in two steps: the first one consists in heating the wine introduced into the boiler in order to obtain two distillate fractions: the brouillis' head and the "brouillis". The brouillis is then brought back to the boiler for a second distillation to obtain four distillate fractions: the heads, the heart, the seconds and the tails. The heart fraction corresponds to the new Cognac spirit that will further undergo a slow maturation in an oak barrel. Cognac distillers use to recycle the seconds fraction in the brouillis of a subsequent second distillation whereas the heads and tails fractions are added in the wine of a subsequent first distillation. No distillate fractions were recycled in the wine nor in the brouillis for this study. The double distillation takes place under thermal conditions that promote the generation of volatile compounds. The aim of this study was to characterize the volatile compounds, usually found in wine and freshly distilled Cognac spirit, formed from the high temperature induced by the distillation process.

## MATERIALS AND METHODS

### Chemicals

The volatile compounds of interest were quantified with reference to a calibration table established with pure standard compounds. These compounds have been found to have an impact on freshly Cognac spirit's quality[11] and are routinely quantified in Cognac spirit by the Bureau National Interprofessionnel du Cognac (BNIC).

Methanol, propanol, isobutanol, 1-butanol, 2-methylbutan-1-ol, 3-methylbutan-1-ol, 1-hexanol, phenyl-2-ethanol, *Cis*-3-hexen-1-ol, ethyl formate, isoamyl acetate, ethyl hexanoate, ethyl lactate, ethyl octanoate, ethyl decanoate, ethyl succinate, isobutanal, furfural, butanal, 2-methylbutanal, pentanal, octanal, trans-2-nonenal, decanal, 1-octen-3-one, linalool, α-terpineol, β-citronellol, 1,1,6-trimethyl-1,2-dihydronaphtalene, β-damascenone, 4-methylpentan-2-ol, ethyl undecanoate, 3,4-dimethylphenol, 4-heptanone, 2,2-dimethylpropanal, O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) were purchased from Sigma-Aldrich-Fluka (St. Quentin Fallavier, France); 1,1,6-trimethyl-1,2-dihydronaphtalene (TDN) was from Interchim (Montluçon, France). Absolute ethanol, pentane, dichloromethane were from VWR International. Sodium chloride was purchased from ACROS Organics (Noisy-Le-Grand, France).

**Raw materials and the distillation process**

An Ugni blanc wine without lees, and having an alcohol strength of 9.5 %v/v and pH 3.3, was used to perform the distillations. A traditional copper pot still was made available by a professional distillery: Distillerie de l'Antenne, S.A.S., 30 rue Gatechien, 16100, Javrezac, France. The elaboration of Cognac spirit requires two distillations at atmospheric pressure. The first step (first heating) consisted in heating 2550 L of wine placed into the boiler at atmospheric pressure with a boiling temperature range from 93 to 100 °C. This step produced the brouillis' head corresponding to the first liters of distillate and the brouillis. This process lasted 11 h. In order to conduct the second heating, 3 wine distillations were necessary to properly load the boiler. From these 3 distillations, 2500 L (corresponding to the boiler's capacity) of brouillis were introduced in the boiler to perform the second distillation. The boiling temperature range inside the boiler was comprised between 82 to 100 °C. During the process, the heads were collected and kept apart. Then came the heart corresponding to the cognac spirit to be aged in oak barrels. Finally, seconds and tails were the two last distillate fractions. This distillation lasted 12 h. **Table 1** shows in detail the different fractions, their volume and alcohol content before and after both distillations.

**Monitoring and sampling during the distillation of Cognac spirit.**

An Endress Hauser LPGmass Coriolis flowmeter (max measured error on volume flow 0.3%) was installed at the distillate output of the pot still. This flowmeter allowed a continuous monitoring of the distillate mass flow, temperature and ethanol concentration. These data were recorded every minute. Before the first distillation, the wine was sampled three times inside the boiler by using the sampling pipe. During the first distillation, heads of brouillis and brouillis were poured in separate tanks. Heads of brouillis, brouillis and stillage fractions were sampled three times for analysis. For the second distillation, the same protocol was followed: before distillation the brouillis in the boiler was sampled three times for analysis and during distillation the fractions (heads, heart, seconds and tails) were poured in separate tanks. Three samples of each distillate fraction and brouillis residual were taken for analysis. For every change of tanks, the volume recorded by the flowmeter was reset which allowed to measure the volume of each fraction indicated in Table 1.The residual volumes contained in the boiler (stillage and brouillis residual) were obtained by subtraction of the distillate fractions.

**Sample preparation and quantitative analysis by gas chromatography**

Volatile compounds such as norisoprenoids and terpenes were present below the limit of quantitation in wine and samples having a low alcohol content (wine residual (stillage), brouillis residual and tails). Therefore, an additional step using laboratory scale distillations was required to concentrate volatile compounds only in these samples. A distillation of wine at atmospheric pressure would lead to a boiling temperature close to 100 °C and would promote the generation of thermal artefacts.[26] In order to prevent these artefacts from occurring, laboratory scale distillations were conducted under low pressure conditions.[26] Moreover, for the stillage, brouillis residual and tails, absolute ethanol was added to reach 9.5 % v/v. (corresponding to the wine's alcohol content). Wine, stillage, brouillis residual and tails samples were then distilled in order to concentrate the volatile compounds using a rotary evaporator. 740 mL of sample were added in a 1 L flask. The temperature of the water-bath was set at 40°C and the pressure was set at 60 mbar. Laboratory scale-distillation was performed until 100 mL of distillate, having a 40 % v/v alcohol content, were obtained. The distillate was then analyzed according to the method used. A solution containing known amounts of volatile compounds of interest were laboratory scale distilled under the same conditions in order to assess the extraction yield of each molecule. These yields were taken into account for the quantitation of volatile compounds in wine, wine residual, brouillis residual and tails samples.

For the analysis of volatile compounds gathered in **Table 2**, three different preparations were performed on all samples: direct injection for major volatile compounds, pentane/dichloromethane extraction for volatile compounds in low concentrations and O-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine hydrochloride (PFBHA) derivatization for carbonyl volatile compounds.

Direct injection for analysis by GC-FID[27]

The direct injection method was used for the analysis of major volatile compounds such as alcohol and esters.[11] The direct injection method was the following: all samples were adjusted to 40 % v/v of ethanol. A Hewlett-Packard 6890 gas chromatograph from Agilent, equipped with a split/splitless injector (220 °C with auto-sampler) and a flame ionization detector (220 °C; $H_2$, 30 mL/min; air, 320 mL/min; makeup gas, $N_2$ at 25 mL/min) was used. The carrier gas was hydrogen with a flow rate of 1.4 mL/min. A CP-Wax 57 CB fused silica WCOT column (50 m × 0.25 mm, 0.25 µm from Chrompack) was used with a split ratio of 1/14. 100 µL of the internal standard 4-methylpentan-2-ol at a concentration of 28 g/L in absolute ethanol were added to 10 mL of sample. Each sample was prepared in triplicate independently and analyzed. The sample volume injected was 0.2 µL and the oven temperature program was the following: 5 min at 35°C, raised at 4 °C/min to 220 °C and then held for 10 min at 220 °C. The identification of compounds was performed by comparing their retention times to those of pure standards. Additional identification was achieved by comparing linear retention indices with the literature. Calibration curves were established with a stock solution prepared with commercially available analytical standards at known concentrations and diluted at different concentrations. Information about the stock solution composition and calibration curve is given in Table 2. Quality verifications were performed periodically to ensure quality control accredited by COFRAC (with reference to ISO 17025 standard), the French laboratories accreditation committee.

Pentane/dichloromethane extraction for analysis by GC-MS

25 mL of sample adjusted to 40 % v/v of ethanol and 2.5 g of NaCl were added to a glass tube. 50 µL of internal standard (ethyl undecanoate: 500 mg/L; 3,4-dimethylphenol: 300 mg/L in absolute ethanol) were added to the solution. For the extraction, 4 mL of pentane/dichloromethane (80:20 v/v) were added to the solution. The sample was then homogenized using a vortex for 3 min. The organic layer (upper layer) was recovered after decantation and was concentrated to 0.3 mL with a Kuderna-Danish apparatus under nitrogen flow. The extract was then analyzed by gas chromatography coupled with a mass spectrometer (GC-MS). For GC analysis, a DB-Wax fused silica WCOT column (60 m × 0.25 mm, 0.25 µm from J&W Scientific) was used. 1 µL of sample was injected in splitless mode and the oven temperature program was the following: 0.7 min at 35 °C, raised at 20 °C/min to 60 °C, then raised at 4 °C/min to 200 °C, then 9° C/min to 243 °C for 45 min. The detector was used in scan mode (m/z 30-300 uma; 5 scans/sec) and Single Ion Monitoring Ion (SIM) mode with an ionization voltage of 70 eV. The temperature of the ion source was set at 230 °C. Identification was performed by comparing the retention index and mass spectra to those of standards when available, and to mass spectra from NIST libraries. Quantitation and semi-quantitation were done by either full scan mode or SIM mode. As previously, calibration curves allowed the quantitation and information about the stock solution, calibration and ion fragments used for quantitation are reported in Table 2.

PFBHA derivatization for carbonyl analysis by GC-MS[18]

To quantitate carbonyl volatile compounds, 10 mL of sample adjusted at 40 % v/v of ethanol and 50 µL of internal standard (4-heptanone at 26.3 mg/L for ketones; 2,2-dimethylpropanal at 26.7 mg/L for aldehydes, both in absolute ethanol) were added in a glass tube. Then, 1 mL of PFBHA at 18 g/L in ultrapure water was added to the solution. The solution was briefly stirred and left to react for 1 hour, away from light. 2 mL of pentane was added and the tube was vortexed for 2 min. The organic phase was collected and reduced to 0.2 mL by using a Kuderna-Danish column under a nitrogen flow. The extract was then analyzed by GC-MS. An Agilent DB5 MS (60 m x 0.25 mm x 1 µm) capillary column was used. A splitless injection of 2 µL of sample was performed. The oven temperature program was the following: 35°C for 0.8 min, raised 10°C/min to 170°C then 3°C/min to 300°C held for 10 min. The chromatographic data were obtained by H-P Chemstation software (Agilent). Identification was performed by comparing the retention time and mass spectra to those of standards. Linear regression was used for quantitation. Information about the calibration are reported in Table 2.

**Statistical analysis**

Data are represented by the mean ± the standard deviation performed on 3 analyzed samples. The hypothesis of the homogeneity of variance was rejected by the Levene test with a significance level of 5 %. Hence, non-parametric Mann-Whitney tests were used in order to ascertain the significant differences between the quantity of a volatile compound before distillation (1st distillation: wine; 2nd distillation: brouillis) and the quantity retrieved after the process (all distillate fractions and liquid remaining in the boiler). All statistical analyses were performed using Microsoft Excel Software.

**Establishing a mass balance of the distillation of Cognac spirit**

An overall mass balance of the volatile compounds previously quantified in wine and each distillate fraction was performed by calculating the volatile compounds' mass present at the beginning in wine and in each fraction (1$^{st}$ distillation: brouillis' head, brouillis, and wine residual; 2$^{nd}$ distillation: heads, heart, 2$^{nd}$, tails, and brouillis residual) throughout the whole distillation process. Thus, a comparison was made between the mass of a volatile compound in the wine before the first distillation and its mass in the resulting fractions, i.e. brouillis' head, brouillis and wine residual. Mass determination of a volatile compound was determined by multiplying the volatile compound's concentration measured in each fraction with its volume. The same principle was applied for the second distillation. Moreover, a mass balance was performed on ethanol in order to assess its recovery ratio during the distillation process. The ethanol content in stillage is known to be under 0.2 % v/v and was considered at 0 % v/v in this study. Regarding the ratio between the volume of ethanol after process and loaded in the boiler, a value of 1.01 for the first distillation and 1.02 for the second distillation were obtained. This mass balance indicates that no loss of ethanol occurred during both distillations (without recycling).

**Evaluating the sensory impact of the distillation process on the heart fraction**

The sensory impact of the charentaise distillation on the heart fraction was estimated for volatile compounds that have increased amounts after the process. The quantity of volatile compound formed during distillation and present in the heart fraction was converted into concentration. This concentration was then compared to odor thresholds reported in the literature when available.

## RESULTS AND DISCUSSION

Establishing mass balances allowed to evaluate the quantitative evolution of the volatile compounds before distillation and afterward. Moreover, the quantitative analysis on each fraction allowed to assess the behavior of each volatile compound during the process. **Table 3** indicates the status of the volatile compounds upon completion of the process. The term "generated" indicates that a compound was not detected in wine and was formed during the distillation process. The term "raised" signifies that a volatile compound was already present in wine but its quantity increased after the completion of the distillation process. The compounds generated or raised are in bold and are discussed in this article. The term "slightly" was used to mark the compound's quantity after distillation as significantly different from its mass before distillation, but having low variations (compounds' mass raised but less than twice their initial mass) or low amounts raised/degraded (involving less than 10 mg in total). The results shown are sorted by chemical family. The mass balance ratio (total mass after distillation divided by the initial mass) is also indicated in Table 3 in parenthesis.

According to Table 3, alcohols remain steady throughout both distillations. This chemical family will not be discussed. For the carbonyl compounds, the mass of 1-octen-3-one is only slightly raised after the first distillation and steady after the second, therefore, only aldehydes are generated or raised upon completion of the process and will be discussed.

**Formation of esters**

Two esters were formed during the distillation process: isoamyl acetate and ethyl succinate. **Figure 1A** shows that the mass of these esters increases during the first heating. Isoamyl acetate was detected in wine but had an increased mass at the end of the first heating. The quantity of ethyl succinate, while under the limit of quantification (LOQ) in wine, was quantitated above the LOQ after the first ditillation. This indicates the raise in quantity of this compound due to the process. Ethyl formate, while not detected in wine, was detected below its limit of quantitation after completion of the first distillation. Thus, the presence of ethyl formate indicates that this compound was formed during the first distillation. The reaction of esterification could take place throughout the distillation process and could explain the augmentation of esters observed. Indeed, the esterification has been shown to occur during the distillation of rum.[28] Ethyl esters were formed from the corresponding carboxylic acid and alcohol, present in excess in wine. 3-methylbutanol and acetic acid are responsible for the formation of isoamyl acetate[29] and were quantified at 0.18 g/L (470 g) and 9.22 g/L (23.5 kg) respectively in wine (data not shown). Hence, the amounts of 3-methylbutanol and acetic acid required to form the esters had a low impact on their mass balances. Although isoamyl acetate seems to be formed upon the first distillation, internal data showed that this compound usually decreases throughout the charentaise distillation. One can imply that the augmentation of isoamyl acetate observed may be specific to the wine used in this study and is not representative of the entire range of wines as a whole.

Thus, **Figure 1B** shows the mass of esters measured in 3 brouillis gathered in the boiler. The mass of isoamyl acetate remained stable while the mass of ethyl succinate slightly decreased. Ethyl formate was not detected in the wine but detected in the brouillis. This suggests that ethyl formate was generated during the first distillation. This compound remained steady throughout the second distillation but was present at low concentrations. Therefore, ethyl formate was not selected for this study. According to the study of Williams,[30] carboxylic acids possess an absolute volatility that favors their presence in the liquid phase rather than in the gas phase. Hence, low amounts of carboxylic acids are present in spirits[31] in comparison to their concentration in wine. The diminished amounts of acids in the brouillis during the second distillation would prevent the reaction of esterification from taking place and would explain the relative stability of the mass of isoamyl acetate. The slight decrease of the mass of ethyl succinate observed in Figure 1B may come from the hydrolysis reaction or from thermal degradation. These observations suggest that the first heating is determinant in esters' formation whereas the second heating has a lower effect.

To have a sensory impact on the Cognac spirit, a newly formed volatile compound must be present in the heart, which corresponds to the Cognac spirit. Thus, **Table 4** presents the repartition of isoamyl acetate and ethyl succinate in the different fractions representing the distillation after completion. Namely, the brouillis' head, brouillis and stillage for the first distillation; the heads, heart, seconds, tails and brouillis residual for the second distillation. At the end of the first distillation, ethyl succinate is exclusively present in the brouillis while isoamyl acetate is mostly found in brouillis but in brouillis' head as well. For the second distillation, Table 4 indicates that isoamyl acetate is mainly found in the heart, meaning that the quantity of this compound formed during the first distillation is present in the Cognac spirit. This observation is in accordance with the studies of Hernández-Gómez *et al*.[32] and Léauté[33] that classified short chain esters in the group of compounds that mainly distill in the head and initial heart fractions because of their low boiling point (i.e. high volatility). Isoamyl acetate has a banana[34]. Isoamyl acetate formed through the charentaise distillation corresponds to an increase of its concentration in the heart of 3.18 mg/L, which is above the isoamyl acetate's odor threshold of

0.245 mg/L determined in whisky.[35] One can expect that this ester, formed during distillation, may contribute to the overall Cognac spirit's aroma. Also, according to the data obtained, only ethyl succinate is present exclusively in the seconds and is then withdrawn from the heart. Lukic *et al*.[36] had noted an analogous behavior for this volatile compound. This compound is characterized by having a high boiling point and polarity and is highly soluble in water, which is one of the main reasons it distilled in the seconds fraction.[33] In the case of a distillation conducted with recycling, the seconds fraction would be added in the brouillis of a subsequent second heating. Due to this recycling, the quantity of ethyl succinate contained in the brouillis could increase and be present in the heart fraction, and therefore, in the Cognac spirit.

**Formation of aldehydes**

According to Table 3, only the masses of isobutanal, furfural and 2-methylbutanal are generated or raised after the first distillation. The mass balances were performed on these compounds and are represented in Figure 1A. Isobutanal, furfural and 2-methylbutanal are not present in wine prior to distillation and are quantified at 3360, 3750 and 690 mg, respectively, at the end of the first heating. These three aldehydes are entirely formed during the first step of the distillation. Strecker degradation can form a series of many Strecker aldehydes, for instance, isobutanal and 2-methylbutanal. Studies have shown that glyoxal and valine are precursors of isobutanal.[37] Moreover, a correlation has been established between heat intensity and isobutanal formation. The higher the intensity, the greater the isobutanal mass found in the brouillis.[37] Furfural can be formed thermally by degradation of a five-carbon monosaccharide, commonly referred to as pentose, and is a pH-dependent reaction.[38] Pentoses could comprise approximately 28% of the reducing sugar content of a dry wine.[39] Among pentoses present in wine, arabinose is reported to occur in highest concentrations, followed by rhamnose.[40] Furfural is a volatile compound having a sweet odor.[41] In Figure 1B, during the second heating masses of isobutanal, furfural and 2-methylbutanal remain unchanged. Pentoses and amino acids do not distillate in the brouillis, therefore they are not present during the second distillation. Thus, the absence of reactants would prevent the Strecker degradation and pentoses degradation from occurring and could explain the steadiness of these three aldehydes during the second heating.

According to Table 4, at the end of the first heating, isobutanal, furfural and 2-methylbutanal are almost exclusively found in the brouillis. However, after the second heating, furfural is present in equal amounts in the heart and seconds while isobutanal and 2-methylbutanal are mainly found in the heart. This observation can be explained by the high boiling point of furfural and its solubility in water. Thus, the furfural's potential sensory impact on Cognac spirit is lessen by the second heating process. In the case of a distillation which recycles the seconds fraction in the brouillis, the furfural contained in the seconds fraction will be added in the brouillis of a subsequent second heating. Thus, this recycling will increase the furfural content in this subsequent brouillis and could lead to an increase of the furfural masses in the heart and seconds. In the end, concentrations of 11.58, 6.53 and 1.87 mg/L were found in the heart fraction, for isobutanal, furfural and 2-methylbutanal respectively. Since isobutanal and furfural were solely generated form the distillation process, and 2-methylbutanal was present at low concentration in wine, one could consider that the concentrations of these three compounds quantified in the heart represent the impact of the distillation on the freshly distilled Cognac spirit. According to the literature, odor thresholds of isobutanal and furfural are 0.0059[35] and 5.80 mg/L[42] in a solution of 40 %v/v of ethanol. For 2-methylbutanal, its odor threshold is estimated at 0.003-0.013 mg/L[43] in water. Hence, these aldehydes could contribute to the overall organoleptic profile of freshly Cognac spirit with isobutanal having a malty[43] aroma while 2-methylbutanal possesses a malty,[43,44] chocolate note.[44]

**Formation of terpenes and norisoprenoids**

Terpenes and norisoprenoids have been identified as important contributors in the freshly distilled Cognac spirit's aroma.[45,46] During the distillation, terpenes and norisoprenoids show a similar evolution and low masses were quantified in comparison with aldehydes and esters. **Figure 2A** shows that the masses of α-terpineol, hotrienol and myrcenol raised after the first distillation. Indeed, 10 mg of α-terpineol were quantified in wine and 60 mg were found upon completion of the first heating. Low amounts of hotrienol and myrcenol were measured in wine while 70 and 35 mg were quantified after the first distillation, respectively. **Figure 2B** indicates that the masses of α-terpineol, hotrienol and myrcenol are steady during the second distillation.

**Figure 3A** shows that the quantities of 12 norisoprenoids are generated or raised during the first heating. In **Figure 3B**, different tendencies can be noted. The masses of actinidol 1 and 2 decrease during the second heating while masses of 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN) and 1-(2,3,6-trimethylphenyl)buta-1,3-diene (TPB) continue to increase. The seven other norisoprenoids remain at steady amounts. Norisoprenoids and terpenes can be present in wine in a glycosylated form.[21,47] The occurrence of glycosidically bound volatile compounds is typically two to eight times greater than that of their free counterparts.[21] Acid hydrolysis under mild conditions (pH = 3) and catalyzed by heat can liberate the volatile compound from its glycosyl moiety.[20,21] Thus, the drastic increase of norisoprenoids and terpenes amounts observed during the first distillation process certainly come from these glycosylated precursors. Moreover, these precursors are not volatile, hence, are not present in the brouillis, which explains the stable quantities of the 7 norisoprenoids and terpenes observed during the second heating step. (E)-1-(2,3,6-trimethylphenyl)buta-1,3-diene (TPB), having floral, geranium and tobacco notes,[48] was found to have an increased quantity after the second heating which indicates that a different type of precursor is involved in its formation. A reaction pathway for the formation of TPB was proposed by Cox et al. (2005)[49] to take place by acid hydrolysis of intermediate megastigma precursors, namely 3,6,9-trihydroxymegastigma-4,7-diene, 3,4,9-trihydroxymegastigma-5,7-diene and isomeric actinidols. Moreover, one can remark the slight decrease of actinidol 1 and 2 during the second heating (Figure 3B), suggesting that they may directly be involved in TPB formation. 1,1,6-trimethyl-1,2-dihydronaphthalene (TDN), having a well-known off flavor of kerosene,[50,51] has an increasing amount throughout both distillations as well. This observation implies that the quantity of TDN is not only raised upon acid hydrolysis of its glycosylated precursors but possesses other precursors involved in its formation, as stated by Strauss *et al.*[52] Indeed, studies proved that Riesling acetal can be a precursor of TDN.[53] By looking at Figure 3, results show that the masse of Riesling acetal remained stable during the second distillation, suggesting that this norisoprenoid does not intervene in TDN formation.

**Table 5** and **Table 6** show that terpenes and norisoprenoids are mainly found in the brouillis fraction, and then in the heart fraction. The concentrations of norisoprenoids and terpenes found in the heart fraction are comprised between 0.02 mg/L for TMPBA and 0.30 mg/L for TDN. Hence, the quantities of norisoprenoids and terpenes formed during the first distillation and finally present in the heart fraction are low. However, their low odor threshold could allow them to have an organoleptic impact on Cognac spirit. For instance, the quantity of hotrienol formed through distillation corresponds to a concentration of 0.23 mg/L in the heart fraction. The odor threshold of this compound was estimated at 0.11 mg/L in water,[54] suggesting that the amount of hotrienol formed potentially has an organoleptic impact on the freshly Cognac spirit. Only actinidols 1 and 2 and 4-(2,3,6-trimethylphenyl)-3-buten-2-one (TMPBE) are found mostly in the seconds fraction. These norisoprenoids follow a similar behavior than furfural. In other words, a charentaise distillation which recycles the seconds fraction in the brouillis will increase the content of actinidols 1 and 2 and TMPBE in the subsequent brouillis and could lead to an increase of the concentration of these compounds in the heart and seconds.

In summary, establishing a mass balance allowed to determine some of the volatile compounds generated during the charentaise distillation process and to assess their presence in freshly distilled Cognac spirit. Thus, 2 esters, 3 aldehydes, 3 terpenes and 12 norisoprenoids were identified as newly formed volatile compounds. In particular, the 4 actinidols, furfural and isobutanal were completely generated by the distillation process. Their presence in the Cognac spirit freshly distilled showed that the distillation process participates in the complex aroma composition of Cognac. Results showed that the first distillation is the decisive step where most of chemical reactions occur. Some volatile compounds with raised concentration during distillation have positive notes (such as isoamyl acetate and 2-methylbutanal) whereas others (such as TDN) could be considered as off-flavors at high concentrations. Characterization of the reactions responsible for the formation of these volatile compounds would allow to determine the kinetic constants that would be embedded into a model to predict their generation. This characterization would also allow to assess the optimal reaction conditions (temperature, pH) that would promote their raise or prevent their formation. Thus, the fact that the first distillation is the most reactive step and knowing the repartition of each volatile compound during the distillation of Cognac spirit can lay the basis for the elaboration of a distillation model that could take the chemical reactions into account.

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## FIGURE CAPTIONS

**Figure 1**. Overall mass balance on esters and aldehydes established before and after both distillations. **A**: first distillation **B**: second distillation. a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples

**Figure 2**. Overall mass balance on terpenes established before and after both distillations. **A**: first distillation **B**: second distillation. a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples

**Figure 3**. Overall mass balance on norisoprenoids established before and after **A**: the first distillation **B**: the second distillation * isomerism not defined ** stereoisomerism not defined. a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples

## TABLES

**Table 1**. Volumes and alcohol content of distillate fractions and the residual solution in the boiler for the first and second distillation as well as mass balance on ethanol (EtOH) for both distillations.

**1st distillation**

| | Load in boiler | After process | | |
|---|---|---|---|---|
| | Wine | Brouillis head | Brouillis | Stillage |
| Volume (L) | 2550 | 4.50 | 834.00 | 1711.50 |
| Alcohol.By.Volume. (%v/v) | 9.50 | 70.33 | 28.82 | < 0.20 |
| Volume of EtOH (L) | 242.25 | 3.17 | 240.36 | 0.00 |
| Mass balance ratio on EtOH | 1.01 | | | |

**2nd distillation**

| | Load in boiler | After process | | | | |
|---|---|---|---|---|---|---|
| | Brouillis | Heads | Heart | Seconds | Tails | Brouillis residual |
| Volume (L) | 2500 | 10.00 | 737.40 | 513.60 | 94.75 | 1144.25 |
| Alcohol By Volume (%v/v) | 28.82 | 82.41 | 70.00 | 39.94 | 5.50 | 0.00 |
| Volume of EtOH (L) | 720.50 | 8.24 | 516.2 | 179.45 | 5.21 | 0.00 |
| Mass balance ratio on EtOH | 0.98 | | | | | |

**Table 2.** Calibration table. [1]Direct injection (FID detection). [2]Pentane/dichloromethane extraction. [3]PFBHA derivatization. [a]Retention index. [b]Limit of quantitation. Std = standard. SQ = Semi-quantified

| Compound | Identification | RI[a] | Ion selected (m/z) for SIM quantitation | Quantitation | LOQ[b] (mg/L) | Relative slope | Intercept | $R^2$ | Linearity range (mg/L) | Stock concentration (mg/L) |
|---|---|---|---|---|---|---|---|---|---|---|
| <u>*ALCOHOLS*</u> | | | | | | | | | | |
| Methanol[1] | Commercial standard | 901 | - | Std | 5.00E-1 | 1.67E-3 | 9.34E-03 | 1.0000 | 1.00 - 200 | 2000 |
| Propanol[1] | Commercial standard | 1041 | - | Std | 5.00E-1 | 2.97E-3 | -1.54E-02 | 1.0000 | 1.00 - 150 | 1500 |
| Isobutanol[1] | Commercial standard | 1104 | - | Std | 5.00E-1 | 3.46E-3 | -1.71E-02 | 1.0000 | 0.50 - 350 | 3500 |
| 1-butanol[1] | Commercial standard | 1152 | - | Std | 5.00E-1 | 3.20E-3 | 5.60E-05 | 1.0000 | 0.50 - 60 | 1200 |
| 2-methylbutan-1-ol[1] | Commercial standard | 1209 | - | Std | 5.00E-1 | 3.80E-3 | -7.76E-02 | 0.9950 | 0.50 - 350 | 3500 |
| 3-methylbutan-1-ol[1] | Commercial standard | 1211 | - | Std | 5.00E-1 | 3.60E-3 | -1.00E-04 | 0.9980 | 0.50 - 950 | 9500 |
| 1-hexanol[1] | Commercial standard | 1356 | - | Std | 5.00E-1 | 3.70E-3 | -6.00E-06 | 0.9970 | 0.50 - 100 | 2000 |
| Phenyl-2-ethanol[1] | Commercial standard | 1921 | - | Std | 5.00E-1 | 4.38E-3 | 4.00E-03 | 1.0000 | 0.50 - 100 | 2000 |
| *Trans*-3-hexen-1-ol[2] | Tentatively identified | 1355 | 67 | SQ with *cis*-3-hexen-1-ol | 6.00E-2 | | | | | |
| *Cis*-3-hexen-1-ol[2] | Commercial standard | 1375 | 67 | Std | 6.00E-2 | 1.88E-1 | 7.21E-03 | 0.9995 | 6.0E-2 - 2.5 | 720 |
| <u>*ESTERS*</u> | | | | | | | | | | |
| Ethyl formate[1] | Commercial standard | 811 | - | Std | 1.00 | 1.39E-3 | 2.00E-05 | 0.9998 | 2 - 75 | 1500 |
| Isoamyl acetate[1] | Commercial standard | 1112 | - | Std | 5.00E-1 | 2.79E-3 | 6.00E-06 | 0.9999 | 0.50 - 50 | 1000 |
| Ethyl hexanoate[1] | Commercial standard | 1224 | - | Std | 5.00E-1 | 2.99E-3 | 1.60E-05 | 0.9999 | 0.50 - 60 | 1200 |
| Ethyl lactate[1] | Commercial standard | 1336 | - | Std | 1.00 | 1.74E-3 | 2.30E-05 | 1.0000 | 1.00 - 150 | 1500 |
| Ethyl octanoate[1] | Commercial standard | 1427 | - | Std | 5.00E-1 | 3.36E-3 | 5.50E-05 | 1.0000 | 0.50 - 75 | 1500 |
| Ethyl decanoate[1] | Commercial standard | 1635 | - | Std | 5.00E-1 | 3.51E-3 | 3.40E-05 | 0.9999 | 0.50 - 150 | 3000 |
| Ethyl succinate [1] | Commercial standard | 1671 | - | Std | 5.00E-1 | 1.93E-3 | 7.00E-06 | 0.9994 | 0.50 - 70 | 1400 |
| <u>CARBONYL</u> | | | | | | | | | | |
| Isobutanal[1] | Commercial standard | 804 | - | Std | 5.00E-1 | 2.98E-3 | -2.31E-03 | 0.9998 | 0.50 - 50 | 1000 |
| Furfural[1] | Commercial standard | 1449 | - | Std | 5.00E-1 | 2.27E-3 | 3.70E-05 | 0.9999 | 0.50 - 60 | 1200 |
| Butanal[3] | Commercial standard | - | 239 + 250 | Std | 3.30E-3 | 8.90E-1 | 0.00 | 1.0000 | 0.00 - 5.6E-2 | 7.49 |
| 2-methylbutanal[3] | Commercial standard | - | 281 + 266 + 253 | Std | 2.00E-1 | 1.73E-2 | 0.00 | 1.0000 | 0.00 - 29.3 | 390.9 |
| Pentanal[3] | Commercial standard | - | 239 + 222 | Std | 6.70E-3 | 1.94 | 0.00 | 1.0000 | 0.00 - 0.047 | 6.2 |
| Octanal[3] | Commercial standard | - | 239 + 222 | Std | 1.00E-3 | 1.66 | 0.00 | 1.0000 | 0.00 - 1.6E-2 | 2.16 |
| *Trans*-2-nonenal[3] | Commercial standard | - | 335 + 250 | Std | 1.00E-3 | 6.60E-1 | 0.00 | 1.0000 | 0.00 - 1.6E-2 | 2.12 |
| Decanal[3] | Commercial standard | - | 239 + 170 | Std | 6.70E-4 | 1.27 | 0.00 | 1.0000 | 0.00 - 2.7E-2 | 3.59 |
| Compound | | RI[a] | Ion selected (m/z) for SIM quantitation | Quantitation | LOQ[b] (mg/L) | Relative slope | Intercept | $R^2$ | Linearity range (mg/L) | Stock concentration (mg/L) |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| 1-Octen-3-one[3] | Commercial standard | - | 321 + 140 | Std | 4.00E-3 | 1.17 | 0.00 | 1.0000 | 0.00 - 5.9E-3 | 0.79 |
| <u>*TERPENES*</u> | | | | | | | | | | |
| Linalool[2] | Commercial standard | 1534 | 71 | Std | 1.70E-2 | 6.10E-1 | 1.84E-4 | 1.0000 | 4.1E-02 - 3.1E-1 | 100 |
| Hotrienol[2] | Tentatively identified | 1595 | 71 + 82 | SQ with β-citronellol | 5.00E-4 | | | | | |
| Myrcenol[2] | Tentatively identified | 1596 | 59 | SQ with β-citronellol | 3.30E-3 | | | | | |
| α-terpineol[2] | Commercial standard | 1688 | 59 | Std | 3.30E-2 | 6.09E-1 | 0.00 | 1.0000 | 4.1E-2 - 3.1E-1 | 100 |
| Terpinene-4-ol[2] | Tentatively identified | 1597 | 154 + 111 | SQ with β-citronellol | 1.70E-3 | | | | | |
| β-citronellol[2] | Commercial standard | 1752 | 95 + 109 | Std | 3.30E-2 | 2.55E-1 | 2.57E-4 | 0.9992 | 2.0E-2 - 1.6E-1 | 50 |
| <u>*NORISOPRENOIDS*</u> | | | | | | | | | | |
| Vitispiranes 1[2] | Tentatively identified | 1531 | 192 | SQ with β-damascenone | 1.30E-2 | | | | | |
| Vitispiranes 2[2] | Tentatively identified | 1534 | 192 | SQ with β-damascenone | 1.30E-2 | | | | | |
| β-cyclocytral[2] | Tentatively identified | 1628 | 152 + 137 | SQ with β-citronellol | 6.70E-3 | | | | | |
| Riesling acetal[2] | Tentatively identified | 1636 | 148 | SQ with β-damascenone | 6.70E-3 | | | | | |
| Actinidol 3[2] | Tentatively identified | 1698 | 163 | SQ with linalool | 1.30E-2 | | | | | |
| Actinidol 4[2] | Tentatively identified | 1728 | 163 | SQ with linalool | 1.30E-2 | | | | | |
| 1,1,6-trimethyl-1,2-dihydronaphtalene (TDN)[2] | Commercial standard | 1743 | 142 | Std | 1.30E-2 | 1.39 | 5.80E-3 | 0.9994 | 9.2E-2 - 6.7E-1 | 200 |
| β-damascenone[2] | Commercial standard | 1818 | 121 | Std | 6.70E-3 | 1.24 | 2.95E-4 | 1.0000 | 5.0E-2 - 4.2E-1 | 130 |
| (*Trans*)-1-(2,3,6)-trimethylphenyl)-buta-1,3-diene (TPB)[2] | Tentatively identified | 1819 | 157 | SQ with TDN | 3.30E-3 | | | | | |
| Actinidol 1[2] | Tentatively identified | 1926 | 163 | SQ with linalool | 1.30E-2 | | | | | |
| Actinidol 2[2] | Tentatively identified | 1939 | 163 | SQ with linalool | 1.30E-2 | | | | | |
| 4-(2,3,6-trimethylphenyl)-butan-2-one (TMPBA)[2] | Tentatively identified | 2222 | 132 | SQ with β-citronellol | 1.70E-3 | | | | | |
| 4-(2,3,6-trimethylphenyl)-3-buten-2-one (TMPBE)[2] | Tentatively identified | 2289 | 173 | SQ with β-citronellol | 1.70E-3 | | | | | |

**Table 3.** List of volatile compounds monitored during the charentaise distillation of Cognac spirit. In bold = the aroma compounds generated during the distillation and studied in this article. [a]Ratio: total mass of volatile compound after distillation / initial mass of volatile compound before distillation. * Quantity involving less than 10 mg despite high ratio.

| Compound | 1st distillation | | | 2nd distillation | | |
|---|---|---|---|---|---|---|
| | Mass in 2550 L of wine (mg) | Mass of compound in 4.50 L heads+ 834 L brouillis + 1711.50 L stillage (mg) | Ratio | Mass for 2500 L of brouillis (mg) | Mass of compound in 10 L heads+ 737.4 L heart+ 513.6L 2nd+ 94.75L tails+ 1144.25L brouillis residual (mg) | Ratio |
| ALCOHOLS | | | | | | |
| Methanol[1] | 96856 | 100299 | 1.04 | 265338 | 272402 | 1.03 |
| Propanol[1] | 85201 | 87596 | 1.03 | 251518 | 265764 | 1.06 |
| Isobutanol[1] | 177828 | 191173 | 1.08 | 543449 | 572971 | 1.05 |
| 1-butanol[1] | 993 | 1011 | 1.02 | 2741 | 2981 | 1.09 |
| 2-methylbutan-1-ol[1] | 120201 | 129473 | 1.08 | 367104 | 380805 | 1.04 |
| 3-methylbutan-1-ol[1] | 466607 | 496793 | 1.06 | 1416871 | 1515531 | 1.07 |
| 1-hexanol[1] | 2914 | 3103 | 1.06 | 8920 | 9150 | 1.03 |
| Phenyl-2-ethanol[1] | 43166 | 47821 | 1.11 | 76652 | 52671 | 0.69 |
| *Trans*-3-hexen-1-ol[2] | 34.9 | 35.7 | 1.02 | 97.5 | 92.6 | 0.95 |
| *Cis*-3-hexen-1-ol[2] | 574.3 | 579 | 1.01 | 1643 | 1656 | 1.01 |
| ESTERS | | | | | | |
| Ethyl formate[1] | N.D. | <LOQ | Generated | 955.8 | 1818 | 1.90 |
| **Isoamyl acetate[1]** | 1400 | 3195 | 2.28 | 5116 | 5279 | 1.03 |
| Ethyl hexanoate[1] | 1169 | 2049 | 1.75 | 2446 | 3085 | 1.26 |
| Ethyl lactate[1] | 431013 | 360128 | 0.84 | 711875 | 623486 | 0.88 |
| Ethyl octanoate[1] | 2392 | 3436 | 1.44 | 5188 | 5451 | 1.05 |
| Ethyl decanoate[1] | 847 | 1393 | 1.65 | 3028 | 3715 | 1.23 |
| **Ethyl succinate [1]** | <LOQ | 585 | - | 1461 | 822 | 0.56 |
| CARBONYL | | | | | | |
| **Isobutanal[1]** | N.D. | 3386 | Generated | 8927 | 10048 | 1.13 |
| **Furfural[1]** | N.D. | 3953 | Generated | 10249 | 10434 | 1.02 |
| Butanal[3] | 2.6 | 9.2 | 3.54 | 21.1 | 14.3 | 0.68 |
| **2-methylbutanal[3]** | <LOQ | 676.8 | - | 1813.0 | 1640 | 0.91 |

| | | | | | | |
|---|---|---|---|---|---|---|
| Pentanal[3] | 6.25 | 14.8 | 2.36 | 46.8 | 38.4 | 0.82 |
| Octanal[3] | 0.31 | 1.1 | 3.48 | 3.7 | 4.6 | 1.23 |
| *Trans*-2-nonenal[3] | 0.07 | 1.3 | 18.43 | 4.5 | 5.7 | 1.27 |
| Decanal[3] | 0.98 | 2.2 | 2.29 | 5.6 | 7.3 | 1.31 |
| 1-Octen-3-one[3] | 0.05 | 0.4 | 7.80 | 1.9 | 1.5 | 0.80 |
| *TERPENES* | | | | | | |
| **Hotrienol[2]** | <LOQ | 71 | - | 197.1 | 192.1 | 0.97 |
| **Myrcenol[2]** | <LOQ | 35 | - | 93.0 | 62.4 | 0.67 |
| **α-terpineol[2]** | 11 | 61 | 5.51 | 159.2 | 158.0 | 0.99 |
| Terpinene-4-ol[2] | <LOQ | 2.6 | - | 10.7 | 11.0 | 1.03 |
| *NORISOPRENOIDS* | | | | | | |
| **Vitispiranes 1 [2]** | <LOQ | 33.6 | - | 87.5 | 93.4 | 1.07 |
| **Vitispiranes 2 [2]** | <LOQ | 28.6 | - | 74.2 | 89.0 | 1.20 |
| β-cyclocytral[2] | <LOQ | 5.7 | - | 15.2 | 15.4 | 1.02 |
| **Riesling acetal[2]** | 1 | 23.2 | 17.80 | 63.3 | 58.6 | 0.93 |
| **Actinidol 3[2]** | N.D. | 11.6 | Generated | 31.7 | 33.1 | 1.05 |
| **Actinidol 4[2]** | N.D. | 8.4 | Generated | 23.3 | 25.0 | 1.07 |
| **1,1,6-trimethyl-1,2-dihydronaphtalene (TDN)[2]** | <LOQ | 57.5 | - | 131.3 | 256.0 | 1.95 |
| **β-damascenone[2]** | 29 | 54.5 | 1.88 | 145.8 | 146.5 | 1.00 |
| **(*Trans*)-1-(2,3,6)-trimethylphenyl)-buta-1,3-diene (TPB)[2]** | N.D. | 5.2 | Generated | 11.7 | 29.7 | 2.55 |
| **Actinidol 1[2]** | N.D. | 121.8 | Generated | 296.7 | 247.1 | 0.83 |
| **Actinidol 2[2]** | N.D. | 161.5 | Generated | 391.7 | 314.8 | 0.80 |
| **4-(2,3,6-trimethylphenyl)-butan-2-one (TMPBA)[2]** | <LOQ | 24.3 | - | 56.4 | 58.7 | 1.04 |
| **4-(2,3,6-trimethylphenyl)-3-buten-2-one (TMPBE)[2]** | <LOQ | 66.1 | - | 148.8 | 135.5 | 0.91 |

**Table 4.** Repartition of each ester and aldehyde shown for every fractions at the end of the first and second distillation. Values of concentrations are given as mean ± SD. The percentage value is obtained by: mass of volatile compound in given fraction / total mass of volatile compound in all fractions.

**1st distillation**

| Compound | Brouillis head | | Brouillis | | Stillage | |
|---|---|---|---|---|---|---|
| ESTERS | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| Isoamyl acetate | 288.75 ± 19.08 | 41.5 | 2.19 ± 0.05 | 58.5 | N.D. | 0.0 |
| Ethyl succinate | N.D. | 0.0 | 0.70 ± 0.06 | 100.0 | N.D. | 0.0 |
| ALDEHYDES | | | | | | |
| Isobutanal | 2.76 ± 0.08 | 0.4 | 4.16 ± 0.24 | 99.6 | N.D. | 0.0 |
| Furfural | N.D. | 0.0 | 4.56 ± 0.09 | 98.1 | N.D. | 1.9 |
| 2-methylbutanal | 1.16 ± 0.18 | 0.8 | 0.84 ± 0.07 | 99.2 | N.D. | 0.0 |

**2nd distillation**

| Compound | Heads | | Heart | | Seconds | | Tails | | Brouillis residual | |
|---|---|---|---|---|---|---|---|---|---|---|
| ESTERS | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| Isoamyl acetate | 58.99 ± 6.67 | 11.3 | 6.41 ± 0.17 | 88.7 | N.D. | 0.0 | N.D. | 0.0 | N.D. | 0.0 |
| Ethyl succinate | N.D. | 0.0 | N.D. | 0.0 | 1.53 ± 0.37 | 95.2 | 1.23 ± 0.75 | 4.8 | N.D. | 0.0 |
| ALDEHYDES | | | | | | | | | | |
| Isobutanal | 151.05 ± 15.96 | 15.0 | 11.58 ± 0.30 | 85 | N.D. | 0.0 | N.D. | 0.0 | N.D. | 0.0 |
| Furfural | 2.73 ± 0.23 | 0.3 | 6.63 ± 0.27 | 46.9 | 9.26 ± 0.07 | 43.6 | 11.76 ± 6.93 | 3.9 | 1.27 ± 0.72 | 5.3 |
| 2-methylbutanal | 23.72 ± 0.98 | 16.2 | 1.87 ± 0.02 | 83.8 | N.D. | 0.0 | N.D. | 0.0 | N.D. | 0.0 |

**Table 5.** Repartition of each terpene shown for every fractions at the end of the first and second distillation. Values of concentrations are given as mean ± SD. The percentage value is obtained by: mass of volatile compound in given fraction / total mass of volatile compound in all fractions.

**1st distillation**

| Compound | Brouillis head | | Brouillis | | Stillage | |
|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| α-terpineol | N.D. | 0 | 6.8E-2 ± 4.3E-3 | 100.0 | N.D. | 0.0 |
| Hotrienol | 2.3E-2 ± 4.0E-2 | 0.2 | 8.4E-2 ± 5.4E-3 | 99.8 | N.D. | 0.0 |
| Myrcenol | 4.60E-3 ± 8.0E-3 | 0.05 | 4.0E-2 ± 1.0E-2 | 94.94 | <LOQ | ≃ 5.0 |

**2nd distillation**

| Compound | Heads | | Heart | | Seconds | | Tails | | Brouillis residual | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| α-terpineol | N.D. | 0.0 | 1.48E-1 ± 5.8E-4 | 69.3 | 9.40E-2 ± 1.5E-3 | 30.7 | N.D. | 0.0 | N.D. | 0.0 |
| Hotrienol | 5.17E-2 ± 5.0E-3 | 0.3 | 2.10E-1 ± 1.2E-2 | 78.8 | 7.18E-2 ± 9.5E-3 | 19.2 | 2.32E-2 ± 2.7E-3 | 2.2 | 1.03E-3 ± 9.8E-4 | 0.6 |
| Myrcenol | 1.41E-2 ± 3.4E-3 | 0.2 | 6.29E-2 ± 1.7E-4 | 74.5 | 3.05E-2 ± 5.2E-3 | 25 | 1.10E-3 ± 9.5E-4 | 0.2 | N.D. | 0.0 |

**Table 6.** Repartition of each norisoprenoid shown for every fractions at the end of the first and second distillation. Values of concentrations are given as mean ± SD. The percentage value is obtained by: mass of volatile compound in given fraction / total mass of volatile compound in all fractions.

**1st distillation**

| Compound | Brouillis head | | Brouillis | | Stillage | |
|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| Actinidol 1 | 4.97E-2 ± 1.44E-2 | 0.2 | 1.22E-1 ± 3.8E-3 | 82.6 | 1.33E-2 ± 7.62E-3 | 17.3 |
| Actinidol 2 | 8.23E-2 ± 2.95E-2 | 0.2 | 1.59E-1 ± 3.8E-3 | 82.2 | 1.78E-2 ± 1.21E-2 | 17.6 |
| Actinidol 3 | 7.00E-3 ± 7.55E-3 | 0.3 | 1.38E-2 ± 1.5E-3 | 99.7 | N.D. | 0.0 |
| Actinidol 4 | N.D. | 0.0 | 1.00E-2 ± 1.05E-3 | 100.0 | N.D. | 0.0 |
| TDN | 5.11E-1 ± 7.1E-2 | 3.1 | 6.60E-2 ± 1.41E-3 | 96.9 | N.D. | 0.0 |
| β-damascenone | 2.05E-1 ± 2.3E-2 | 2.2 | 6.40E-2 ± 3.30E-3 | 97.8 | N.D. | 0.0 |
| Riesling acetal | N.D. | 0.0 | 2.76E-2 ± 1.07E-3 | 100.0 | N.D. | 0.0 |
| Vitispirane 1 | 1.48E-1 ± 0.00 | 2.0 | 3.94E-2 ± 3.38E-3 | 98.0 | N.D. | 0.0 |
| Vitispirane 2 | 1.44E-1 ± 1.4E-2 | 2.3 | 3.35E-2 ± 8.10E-4 | 97.7 | N.D. | 0.0 |
| TPB | 5.93E-2 ± 1.4E-2 | 5.9 | 5.96E-3 ± 2.58E-3 | 94.1 | N.D. | 0.0 |
| TMPBA | 2.21E-2 ± 9.1E-3 | 0.4 | 2.50E-2 ± 2.06E-3 | 85.5 | 1.99E-3 ± 5.70E-4 | 14.1 |
| TMPBE | 9.63E-2 ± 3.9E-2 | 0.7 | 6.80E-2 ± 2.54E-3 | 85.7 | 5.26E-3 ± 1.26E-3 | 13.6 |

**2nd distillation**

| Compound | Heads | | Heart | | Seconds | | Tails | | Brouillis residual | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| Actinidol 1 | N.D. | 0.0 | 6.23E-2 ± 1.5E-3 | 18.6 | 3.39E-1 ± 7.9E-3 | 70.6 | 0.12 ± 9.15E-2 | 4.6 | 1.35E-2 ± 5.91E-3 | 6.2 |
| Actinidol 2 | <LOQ | ≃ 0.02 | 7.77E-2 ± 2.5E-3 | 18.2 | 4.29E-1 ± 1.1E-2 | 70.3 | 0.16 ± 0.12 | 4.7 | 1.91E-2 ± 9.83E-3 | 6.8 |
| Actinidol 3 | N.D. | 0.0 | 4.40E-2 ± 0.0 | 100.0 | N.D. | 0.0 | N.D. | 0.0 | N.D. | 0.0 |
| Actinidol 4 | N.D. | 0.0 | 3.30E-2 ± 0.0 | 100.0 | N.D. | 0.0 | N.D. | 0.0 | N.D. | 0.0 |
| TDN | 2.85 ± 0.4 | 11.1 | 2.99E-1 ± 2.7E-3 | 86.1 | 1.17E-2 ± 6.35E-3 | 2.3 | N.D. | 0.0 | N.D. | 0.0 |
| β-damascenone | 3.77E-2 ± 4.9E-3 | 0.3 | 1.78E-1 ± 1.2E-3 | 89.8 | 2.77E-2 ± 5.80E-4 | 9.7 | N.D. | 0.0 | N.D. | 0.0 |
| Riesling acetal | 9.33E-3 ± 5.1E-3 | 0.2 | 6.77E-2 ± 1.2E-3 | 85.2 | 1.60E-2 ± 0.00 | 14.0 | <LOQ | ≃ 0.7 | N.D. | 0.0 |
| Vitispirane 1 | 8.45E-1 ± 1.1E-1 | 9.1 | 1.12E-1 ± 3.1E-3 | 88.2 | <LOQ | ≃ 2.7 | <LOQ | ≃ 0.0 | N.D. | 0.0 |
| Vitispirane 2 | 7.16E-1 ± 1.4E-1 | 8.1 | 1.08E-1 ± 2.7E-3 | 89.5 | <LOQ | ≃ 2.4 | N.D. | 0.0 | N.D. | 0.0 |

| Compound | Heads | | Heart | | Seconds | | Tails | | Brouillis residual | |
|---|---|---|---|---|---|---|---|---|---|---|
| | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) | Concentration (mg/L) | Percentage (%) |
| TPB | 0.21 ± 2.9E-2 | 7.1 | 3.60E-2 ± 0.0 | 89.4 | <LOQ | ≃ 3.46 | N.D. | 0.0 | N.D. | 0.0 |
| TMPBA | 7.63E-3 ± 1.3E-3 | 0.6 | 2.08E-2 ± 5.1E-4 | 98.1 | 7.81E-2 ± 5.3E-4 | 0.99 | 2.18E-2 ± 4.2E-3 | 0.1 | <LOQ | ≃ 0.3 |
| TMPBE | 3.64E-2 ± 4.5E-3 | 0.1 | 6.02E-2 ± 1.3E-3 | 26.2 | 0.17 ± 3.0E-3 | 68.3 | 1.87E-2 ± 1.7E-3 | 3.5 | 2.25E-3 ± 1.7E-4 | 1.9 |

## FIGURES

**Figure 1**. Overall mass balance on esters and aldehydes established before and after both distillations. **A**: first distillation **B**: second distillation. a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples

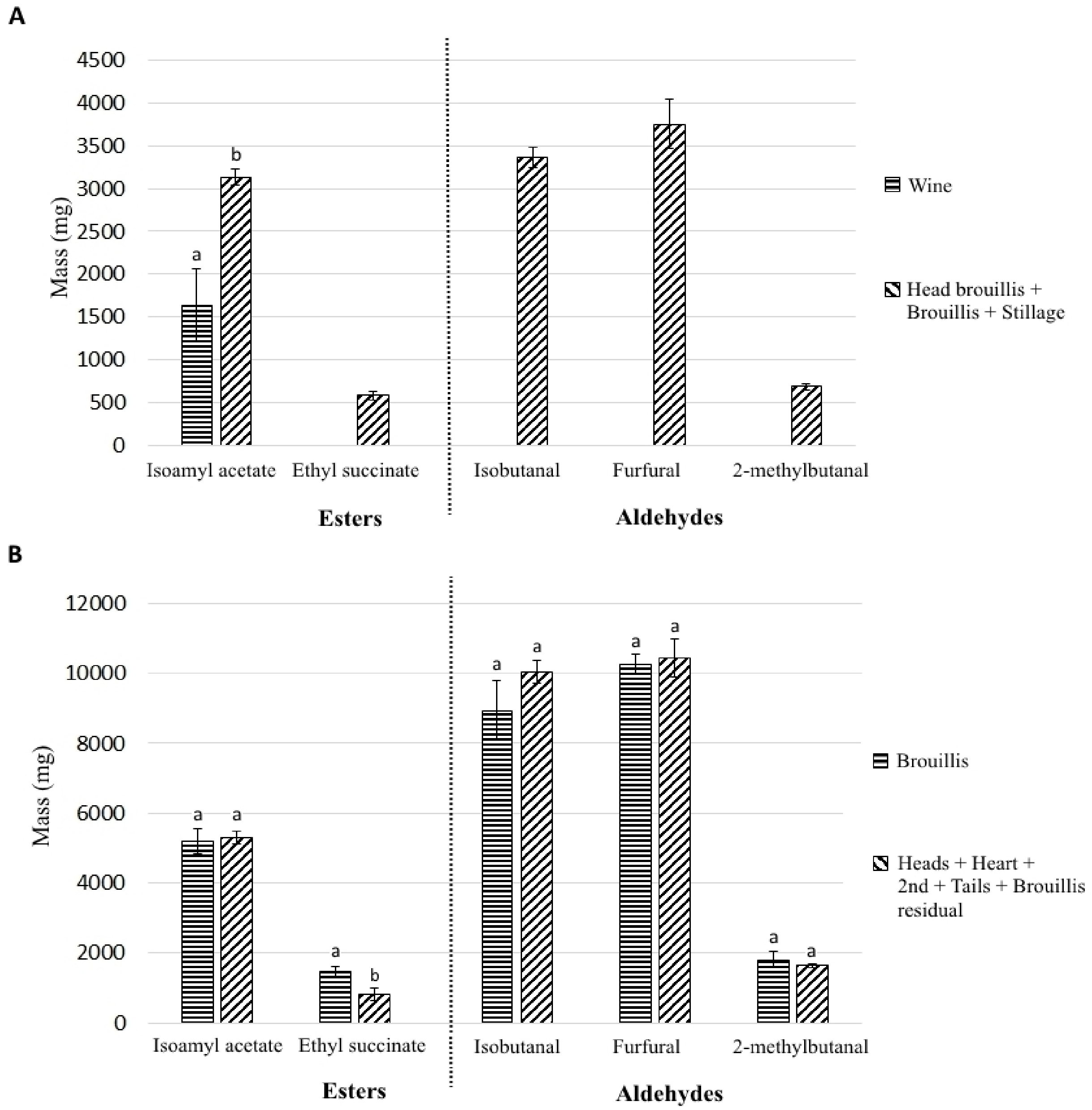

**Figure 2**. Overall mass balance on terpenes established before and after both distillations. **A**: first distillation **B**: second distillation. a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples

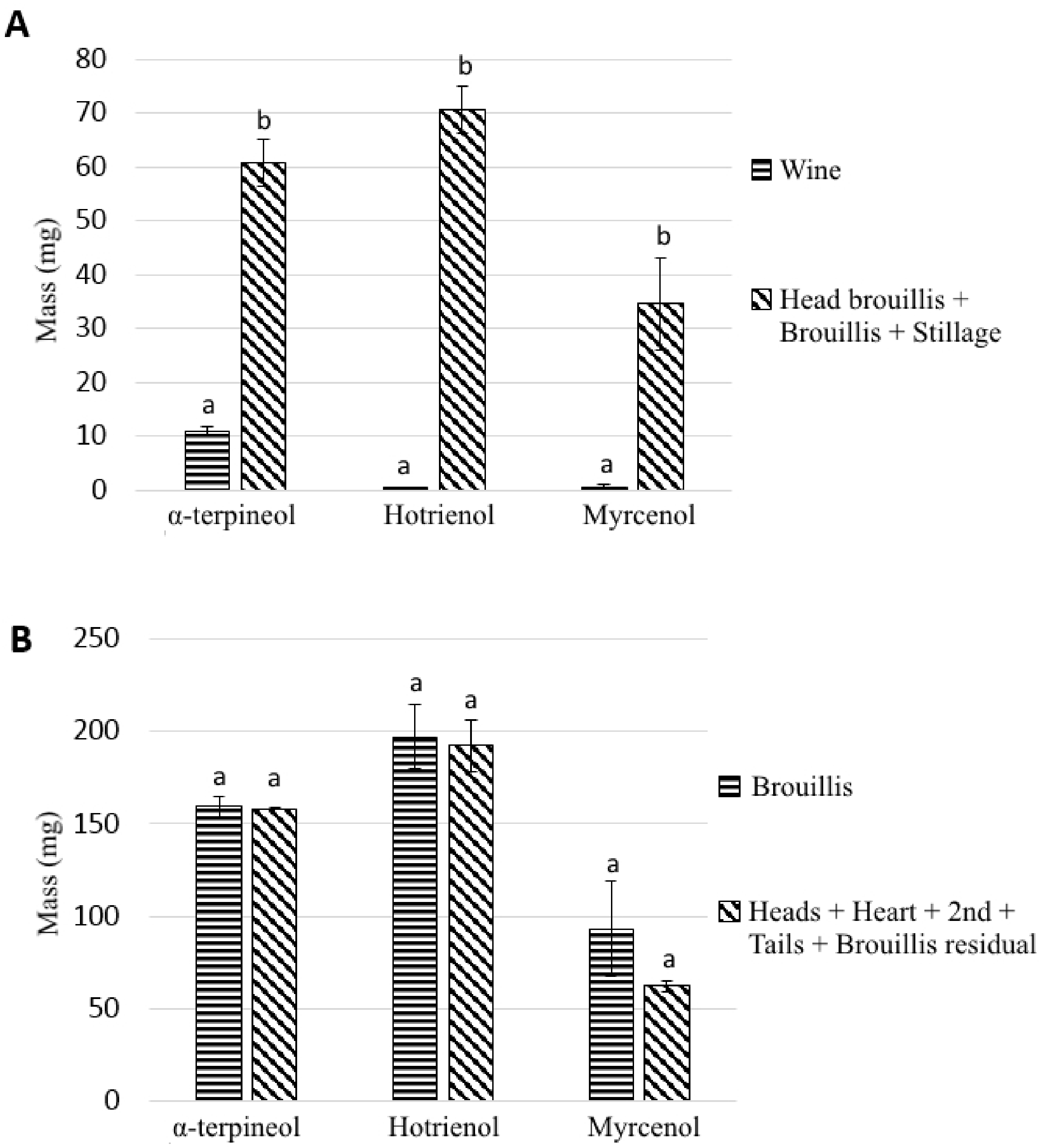

**Figure 3**. Overall mass balance on norisoprenoids established before and after **A**: the first distillation **B**: the second distillation * isomerism not defined **stereoisomerism not defined a a = no significant differences quantities of a volatile compound before and after the distillation process. a b = significant differences between quantities of a volatile compound before and after the distillation process. Error bars: standard deviation performed on 3 analyzed samples