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Influence of Terroir on the Grain Composition, and Volatile Profile of Irish Grain (Wheat) New Make Spirit

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Abstract: Terroir refers to the combination of environmental factors, such as climate, soil, and agricultural practices, that shape the characteristics of a crop, contributing to the unique qualities of the final product. The concept has been traditionally linked to wine, but some recent findings suggest that it also holds importance for distilled spirits. The expanding Irish distilling sector is shifting towards local raw materials such as wheat and rye, driven by regulatory changes, economic benefits, and consumer demand for sustainable local products. This research examines the effects of wheat variety, geographical location, and harvest year on grain composition and volatile composition of the new make spirit. For this study, twenty lab-scale wheat whiskey samples were produced from five different wheat varieties grown at two different locations in Ireland over two consecutive years. The wheat samples were analysed for grain composition and the volatile profiling of new make spirit samples by headspace solid-phase microextraction (HS-SPME) followed by gas chromatography–mass spectrometry (GC-MS). A total of fifty-one volatile compounds were detected, with ethanol, ethyl acetate, phenyl ethyl alcohol, and 3-methyl-1-butanol being predominant. Principal component analysis revealed that both the harvest year and geographical location moderately influenced the volatile compound distribution of the new make spirit, which is explained by a 43.25% variance. ANOVA analysis revealed that grain composition was significantly influenced by harvest year, location, and wheat variety. The 2020 samples showed higher protein and β-glucan content, whereas samples from the location Tipperary had higher starch content. This study indicates that terroir—specifically seasons (year) and geography (location)—affects the characteristics of wheat-based Irish whiskey, highlighting opportunities for distillers to differentiate their products by leveraging local environmental factors.

Keywords: Irish whiskey; volatile organic compound; wheat variety; terroir; GC-MS

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Citation: Vashishtha, A.; Kilcawley, K.N.; Skibinska, I.; Whelan, S.; Byrne, J.L.; Garcia-Cabellos, G.; Morris, S. Influence of Terroir on the Grain Composition, and Volatile Profile of Irish Grain (Wheat) New Make Spirit. *Beverages* **2024**, *10*, 106. https://doi.org/10.3390/beverages10040106

Academic Editors: Ana Leahu, Marìa Soledad Prats Moya and Cristina Ghinea

Received: 10 October 2024
Revised: 29 October 2024
Accepted: 4 November 2024
Published: 5 November 2024

1. Introduction

The Irish whiskey sector is experiencing a renaissance characterised by rapid growth and innovation, with an increasing emphasis on local raw material and grain diversity. For decades, imported maize dominated the Irish distilling business, particularly in the production of blended whiskey, which is by far the largest volume of whiskey style produced and exported from Ireland. Notably, grain whiskey constitutes approximately 80% of all blends and is traditionally made using maize. However, the Irish technical file, which sets out the geographical area covered by the GI and the systems and materials used in the production of Irish whiskey, is currently under review because future regulations may require Irish grain whiskey to be produced solely from the locally produced grains. To accommodate these anticipated changes and the expansion in the distilling sector, there is a growing need to explore alternative grains such as wheat, especially due to the high production of Irish wheat [1]. Ireland produces 0.68 million tonnes of wheat per year, a production volume high enough to make it a suitable candidate as an alternative grain [2]. The promotion of local grains can also significantly enhance rural economic growth and provide stable employment opportunities [3]. This shift to alternative crops reflects not only the dynamic nature of the industry but also the evolving economic landscape and the pressing need for distilleries to distinguish their service in a crowded market. Amidst this context, the concept of terroir emerges as a potential unique selling point (USP), offering a novel dimension to the narrative and marketing of the new whiskey product [4]. These evolving factors create the framework for further investigation of the elements that make Irish whiskey unique, with an emphasis on understanding the role of terroir in shaping its flavour.

Terroir, a French term traditionally associated only with wine, consists of the influence of a locale's environmental characteristics, such as climate, topography, and soil composition, on the phenotype of crops, therefore affecting the flavour profile of the end product derived from them [5,6]. The concept has been extensively applied to wine, with research suggesting a molecular correlation between terroir and the unique characteristics of wines. Just as in wine, in the beer industry, the influence of barley genotype on sensory descriptors has demonstrated terroir's significance in affecting how the flavour ranges from cereal and floral to malty and fruity [7,8]. Based on these foundations and existing research, recent studies have expanded the application of terroir to distilled beverages, including whiskey [9,10]. Given the growing interest in grain diversity and local sourcing within the industry, the investigation of terroir's impact on whiskey production is very pertinent. The interest is not only driven by the quest for quality and authenticity but also by the strategic and marketing need to differentiate products in a highly competitive environment.

The intricate process of whiskey production, from grain selection to maturation, can significantly influence the sensory attributes of the final product. Factors such as the selection of raw materials and production processes such as malting, mashing, distilling, and, most importantly, maturation shape the whiskey's flavour [11]. Esters primarily produced during alcoholic fermentation by yeast infuse the whiskey with fruity and floral notes, such as those of ethyl hexanoate and isoamyl acetate, while alcohols derived both directly from the raw materials and produced during the malting process, add to the whiskey's complexity [12]. The malting process, through a sequence of enzymatic reactions known as the lipoxygenase pathway, transforms lipids in the presence of oxygen to produce distinctive alcohols such as hexanol. Additional alcohols, including 2-methyl-1-butanol and 3-methyl-1-butanol, emerge during fermentation, further diversifying the spirit's aromatic profile [13]. The maturation process in casks is another critical phase where the new make spirit acquires depth, character, and a harmonious blend of flavours; however, these aspects during maturation are beyond the scope of this study. Gas chromatography–mass spectrometry (GCMS) is widely used to identify volatile compounds in distilled spirits, providing a greater understanding of aromatic components generated from the grains or the production processes [14,15].

Critics of terroir may argue that the distillation process can mask the subtle influences of the original raw material. However, some previous research on barley and maize whiskey have shown that if the production parameters are kept constant, there is a measurable variance in the whiskey flavours, attributable to the different grain types, and grain production environment/geography, reinforcing the idea that terroir does indeed play a critical role in shaping the sensory profiles of whiskey. By investigating the effects of the wheat varieties harvested over two consecutive years in distinct Irish locations, such as Carlow and Tipperary, this paper seeks to contribute to the ongoing debate on terroir in whiskey, aiming to elucidate its potential as a distinctive selling point in the evolving landscape of the Irish whiskey sector.

The overarching aim of this research is to study the effect of terroir factors such as season (year), geography (location), and crop variety on the grain composition and volatile profile of Irish Whiskey. In the subsequent sections, we will be discussing the methodology, results, and discussions centered around the findings of the above objective.

2. Materials and Methods

2.1. Grain Samples

Wheat samples were sourced from field-based research trials by Teagasc, Oak park Rd, Oakpark Or Painestown, Carlow. These included the following varieties: Revelation, Viscount, Elation, Torp, and LG Astronomer, collected from two different locations (Carlow and Tipperary, Ireland) and across two harvest years (2020 and 2021).

In this study, the two different locations from where the crops were harvested (Carlow and Tipperary) differ in the environment, making the location a suitable factor for terroir analysis. Carlow, located in the southeast of Ireland, enjoys a temperate maritime climate characterised by mild winters and cool summers due to its position in the "Sunny South-east". This climate, combined with a mix of fertile alluvial soils along the Barrow Valley and patches of stonier land, makes it suitable for a diverse range of agricultural practices. Alternatively, Tipperary, situated in the midwest and part of the Golden Vale, experiences slightly cooler temperatures and more precipitation, influenced by its varied topography, including several mountain ranges. The soils here are predominantly deep, fertile, and well-drained, enriched by limestone, which is ideal for intensive agricultural operations.

2.2. Grain Composition Analysis

The grain composition analysis was conducted to quantify the levels of β-Glucan, arabinoxylans, protein, and starch within the wheat samples. Protein measurements were taken using a whole grain analyser (Infratec 1241 grain analyser; Foss Tecator AB, Hoganas, Sweden).

- β-Glucan, Arabinoxylans, and starch analysis:

The quantification of β-glucan K-BGLU, SKU: 700004269, Arabinoxylans, and total starch using a Total starch assay kit (K-TSTA-100A; SKU: 700004351) was performed using specific assay kits supplied by Megaenzyme (Bray, Ireland). All the samples were analysed in triplicate, and their average mean and standard deviation values were recorded, as referred to in Table A2, Appendix A. The methodology for each component was executed according to the manufacturer's protocols.

- Moisture content determination:

The samples were first grounded using a Buhler Miag disc mill (Buhler Group Dublin, Ireland) to achieve the mean particle size of 0.2 mm. The moisture content method of the wheat was adapted from the European Brewing Convention (EBC: 6.2.2) [16] method for measuring the moisture content of maize. Approximately 5 g of the ground grain sample was spread evenly in a thin layer in pre-weighed aluminium moisture dishes about 50 mm in diameter and not more than 20 mm in depth. The samples were then dried in an oven set at 130–135 °C for 1 h. After drying, the moisture was calculated based on the weight difference before and after drying, using the following Equation (1).

$$Moisture\ content\ (\%) = \frac{Initial\ weight - Dry\ weight}{Initial} \times 100 \quad (1)$$

2.3. Whiskey Sample Preparation

Whiskey samples were prepared using the method adopted by Morris et al., 2022, [1], which simulated the "typical" lab-scale production of Irish whiskey. Wheat flour (30 g) was obtained by milling the grains in a Buhler Miag Disc mill (setting 0.2 mm) (Buhler Group, Dublin, Ireland). The flour was then transferred to the mash utensils and slurried with water (86 mL preheated to 40 °C), with the addition of α-amylase (39.6 μL, Kerry

BiofermTM LC Alpha-amylase, sourced from BSG CraftBrewing) and 141 mg/L ca ions in the form of calcium chloride dihydrate (CaCl2·2H2O; ranged from 0–733.66 mg/L; PanReac Appliedchem ITW reagents, Dublin, Ireland). The contents were gradually heated to 78 °C (temperature rises to 2 °C/min) in a water bath and cooked for 123 min. The cooked slurry was then cooled to 66 °C and given a second treatment of α-amylase (14.4 µL, Kerry BiofermTM LC Alpha-amylase, sourced from BSG CraftBrewing), and amyloglucosidase (26.5 µL, AmyloTM 300, sourced from BSG CraftBrewing). This was mashed with an inclusion rate of 5% using high diastatic power-distilling malted barley (cv. Laureate, Miag setting 0.2 mm). After this step, the mash was cooled to 40 °C, followed by additional β-Glucanase (45 µL BioglucanaseR GB sourced from BSG CraftBrewing), and the mash was allowed to rest for 60 min. The mash was then cooled to 22 °C and was made up to 250 mL with water. After this, all the samples were fermented with distillers' yeast (Pinnacle 'M' type) at a pitching rate of 0.4% for 72 h. The fermented wort samples were distilled using the EBC Method 9.2.1 [17] in a still steam distillation apparatus. The final ABV% for the final samples was read on an Anton Paar 5000 density meter (Anton Paar, Dublin, Ireland), which was not more than 10% for any sample, preventing further dilution at the stage of volatile analysis using headspace solid phase microextraction (HS-SPME) GC-MS analysis. The distillates/fresh-made spirits were stored in sterile falcon tubes. The samples were stored under optimal conditions in a 0–5 °C refrigerator to preserve the chemical integrity for subsequent analysis.

2.4. Volatile Profile Analysis

- HS-SPME GCMS analysis

Twenty whiskey samples were analysed in triplicates for volatile components using headspace solid-phase microextraction gas chromatography–mass spectroscopy; sample IDs are shown in Table A1, Appendix A. The ABV% of these samples post-distillation was measured using an Anton Paar 5000 density meter (Anton Paar, Dublin, Ireland), which is also recorded in Table A1.

- SPME: Sample preparation

A 5 mL sample and 100 µL standard (4-methyl, 2-pentanol, and 2-methyl, 3-heptanone at 10 ppm) sample were added to a 200 mL screw-capped amber SPME vial with a magnetic cap and silicone/polytetrafluoroethylene septa (Element, Maynooth, Ireland) and equilibrated to 40 °C for 10 min with pulsed agitation of 5 s at 500 rpm. The sample was introduced using a Gerstel MPS autosampler.

- GCMS Method

A single 50/30 µm CarboxenTM/divinylbenzene/polydimethylsiloxane (DVB/CAR/PDMS) fibre was used (Agilent Technologies Ltd., Cork, Ireland). The SPME fibre was exposed to the headspace above the samples for 40 min at a depth of 1 cm at 40 °C. The fibre was retracted and injected into the GC inlet and desorbed for 2 min at 250 °C. Injections were made on a Shimadzu 2010 Plus GC (Mason Technology, Dublin, Ireland) with a DB-624 UI (60 m × 0.32 mm × 1.8 µm) (Agilent Technologies Ltd.) column using a split/split less injector with a 1/10 split. A Merlin micro seal was used as the septum (Agilent Technologies Ltd.). The temperature of the column oven was set at 40 °C, held for 5 min, increased at 5 °C/min to 230 °C, then increased at 15 °C/min to 260 °C, and held for 15 min, yielding a total GC run time of 60 min. The carrier gas was helium, held at a constant flow of 1.2 mL/min. The detector was a Shimadzu TQ8030 mass spectrometer detector (Mason Technology), run in single quad mode. The ion source temperature was 220 °C, and the interface temperature was set at 260 °C. The MS mode was electronic ionisation (70 v) with the mass range scanned between 35 and 250 amu. Compounds were identified using mass spectra comparisons to the NIST 2014 mass spectral library, a commercial flavour and fragrance library (FFNSC 2, Shimadzu Corporation, Japan), and an in-house library created using authentic compounds with target and qualifier ions and linear retention indices (LRI) for each compound using Kovats index [18]. Spectral deconvolution was also performed to confirm the identification of compounds using AMDIS [19]. Batch processing of samples was carried out using MetaMS [20]. MetaMS is an open-source pipeline for GC-MS-based untargeted metabolomics. An auto-tune of the GCMS was carried out before the analysis to ensure optimal GCMS performance. A set of external standards was run at the start and end of the sample set, and abundances were compared to known amounts to ensure that both the SPME extraction and MS detection were performed within specifications.

2.5. Statistical Analysis

Statistical analysis was carried out using R studio, R version 4.2.2 (2022-10-31 ucrt) [21] for principal component analysis (PCA), normality test, constant variance test, and statistical analysis of variability (ANOVA). Three-way ANOVA was conducted to determine if there were statistically significant differences in the grain composition and volatile profile based on factors such as wheat variety, geographical location, and harvest year and due to the interaction of these factors. Turkey's post hoc HSD was conducted on the most significant factors that affected the grain composition. PCA was used for volatile profile analysis because of its ability to reduce the dimensionality of large data sets, help identify clusters, and visualise how different terroir factors influence the samples' characteristics.

3. Results and Discussion

The following section includes the results of the effect of terroir factors, such as season (year), geography (location), and wheat variety, on grain composition and volatile profile of whiskey.

3.1. Grain Composition Analysis

The effect of variety, location, and year on the response variables—protein, β-glucan, and arabinoxylans—was evaluated using a three-way ANOVA, followed by post hoc analysis using Turkey's HSD. Before conducting the ANOVA, the assumptions of normality and homogeneity of variance were assessed for all response variables. Normality was evaluated using the Shapiro–Wilk test. The results indicated that protein and β-glucan required log transformations to meet normality assumptions, while starch and arabinoxylans were sufficiently normal. Homogeneity of variance was assessed using Levene's test, which confirmed that the variances were homogeneous across groups for each variable.

Statistical Analysis of Variability

ANOVA was conducted to assess the significance of the influence of site (Tipperary and Carlow), variety (LG Astronomer, Torp, Viscount, Elation, and Revelation), and harvest year (2020 and 2021) on the grain composition, as summarised in Table 1 below.

From the above table, it can be concluded that the protein content is primarily affected by the harvest year and wheat variety, which suggests that both the genetic makeup of the crop and climatic conditions during each harvest season play an important role in determining protein levels. There was a significant interaction between varieties and location, suggesting that the impact of variety on protein content depended on the location where it was grown. It aligns with the literature, which suggests that geography is known to affect the protein components of wheat, majorly gliadin and glutenin [22]. Additionally, interactions between variety and year, as well as location and year, were also significant. Post hoc analysis revealed that Torp and revelation had a higher protein content than Elation, and protein content was significantly lower in samples from 2021 than in 2020.

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Table 1. ANOVA results for the effects of year, variety, and site on the composition of wheat grain.

Response Variable	**Source**	**Df**	**Sum Sq**	**Mean Sq**	**F value**	**Pr (>F)**
Protein	Variety	4	0.05	0.01	15.10	1.78×10^{-7} ***
	Location	1	0.0	1×10^{-5}	0.01	0.91
	Year	4	0.05	0.12	153.55	$<2 \times 10^{-16}$ ***
	Variety: Location	3	0.02	0.01	6.76	0.00091 ***
	Variety: Year	3	0.01	0.01	3.91	0.01 *
	Location: Year	1	0.01	0.01	21.81	3.70×10^{-5} ***
	Variety: Location: Year	3	0.01	0.00	2.31	0.09
	Residuals	38	0.03	0.00		
Beta Glucan	Variety	4	0.56	0.14	5.7	0.001076 **
	Location	1	2.85	2.85	114.74	4.88×10^{-13} ***
	Year	4	0.76	0.19	7.72	0.000118 ***
	Variety: Location	3	0.33	0.11	4.47	0.008769 **
	Variety: Year	3	0.77	0.25	10.36	4.04×10^{-5} ***
	Location: Year	1	0.32	0.32	12.96	0.000905 ***
	Variety: Location: Year	3	0.36	0.12	4.95	0.005355 **
	Residuals	38	0.94	0.02		
Starch	Variety	4	1288.9	322.2	8.77	4.06×10^{-5} ***
	Location	1	2213.0	2213.0	60.23	2.36×10^{-9} ***
	Year	4	727.9	182.0	4.95	0.00259 **
	Variety: Location	3	372.2	124.1	3.38	0.02806 *
	Variety: Year	3	161.1	53.7	1.46	0.24
	Location: Year	1	0.4	0.4	0.01	0.91
	Variety: Location: Year	3	296.3	98.8	2.69	0.06
	Residuals	38	1396.2	36.7		
Arabinoxylans	Variety	4	363.0	90.74	17.48	3.24×10^{-8} ***
	Location	1	31.3	31.26	6.02	0.01883 *
	Year	4	123.2	30.81	5.93	0.000821 ***
	Variety: Location	3	128.9	42.97	8.28	0.000231 ***
	Variety: Year	3	51.9	17.31	3.335	0.029365 *
	Location: Year	1	199.9	199.9	38.509	2.97×10^{-7} ***
	Variety: Location: Year	3	215.5	71.83	13.839	2.99×10^{-6} ***
	Residuals	38	197.3	5.19		

Significance level: ***: $p < 0.001$, highly significant; **: $0.001 \leq p \leq 0.01$, moderately significant, *: $0.01 \leq p \leq 0.05$, significant.

Starch content, on the other hand, was significantly influenced by all the factors (variety, location, and year). Factors such as environmental conditions, including temperature, rainfall, and soil characteristics, play a critical role in determining the synthesis and quality of starch in wheat grains. Studies have shown that even environmental stress factors, such as heat and drought, can directly impact starch metabolism by altering the enzyme activity during crucial periods like anthesis and grain filling, which in turn affects starch composition and quality across different years [23]. Additionally, factors such as variation in the timing of sowing and the specific environmental conditions during different seasons have also been found to significantly alter starch properties, such as viscosity and thermal characteristics, indicating the importance of site-specific agricultural practices and seasonal timing [24]. Post hoc analysis revealed that the starch content in Tipperary was significantly higher than that in Carlow.

For the non-starch polysaccharides (arabinoxylans and β-Glucan), all factors, such as wheat variety, location of harvest, and harvest year, had a significant effect, and even the interaction effect between all three factors was significant for the non-starch polysaccharides. Tipperary showed a significantly lower β-glucan content compared to Carlow, and 2021 samples had lower β-glucan content compared to 2020.

While the above findings suggest an influence of environmental factors as an integral part of terroir, additional factors such as soil nutrient composition might also play a role, highlighting the complex interplay of environmental influence.

3.2. Volatile Profile Analysis

In this section, the distribution of the volatile profiles was studied to determine the effect of terroir factors such as season (year), geography (location), and wheat variety.

In total, 51 volatile compounds were identified in the twenty newly made spirit samples (Tables A3 and A4—Appendix A). The aroma profile consisted of acetals (2), alcohols (12), aldehydes (9), benzenes (2), esters (19), ethers (1), furan (1), ketones (3), lactone (1), phenol (1).

The volatile compounds in Tables A3 and A4 in Appendix A offer a detailed volatile structure of the new-made samples, which were used for multivariate analysis. Ethanol, ethyl acetate, phenylethyl alcohol, 3-methyl-1-butanol, and 2-methyl-1-butanol were identified as the most abundant volatiles across the samples. Ethanol is the main alcohol in all distillates, so it was expected to be a dominant compound (the abundance of ethanol is not a reflection of the true ethanol content as the sample was introduced as a 1:20 split onto the GCMS so as not to saturate the column and detector with ethanol to prevent ethanol overlapping with other early eluting volatile components). Ethyl acetate, with its sweet and fruity attributes, was prominent, adding to the complex sensory profile of the whiskey. The concentration of ethyl acetate is indicative of a balance between yeast metabolism and the conditions during fermentation and distillation [25].

Phenylethyl alcohol, known for its rose-like honeyed odour profile, was also detected in significant quantities. This aromatic alcohol is associated with higher perceived aromatic complexity and quality in distilled spirits [26]. The higher alcohols, or fusel alcohols, such as 3-methyl-1-butanol and 2-methyl-1-butanol, are important components due to their impact on the overall character of the spirit. These compounds are often linked to malty and roasted sensory notes, contributing to the complexity of the aroma. Their concentration can serve as an indicator of yeast metabolism during fermentation, as well as the quality and characteristics of the raw material employed [27].

Principal Component Analysis

The analysis helped in examining clusters formed by whiskey in regards to the distribution of volatile compounds based on the location, year, and variety, as shown in Figure 1.

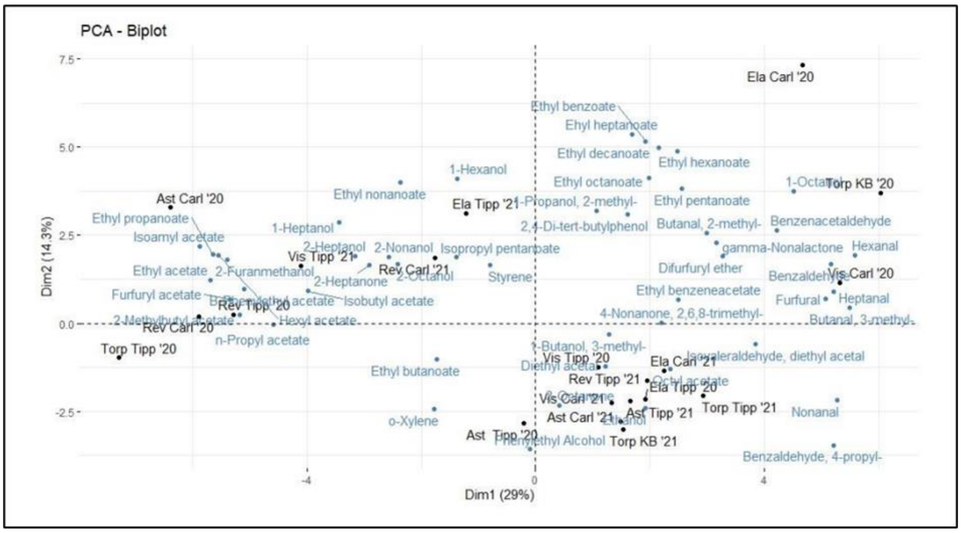

Figure 1. PCA Bi plot of separation based on the volatile profile (samples + volatiles); sample IDs present in Table A1.

Figure 1 presents a PCA plot, where each point represents an individual whiskey sample plotted against the first two principal components (PC1 and PC2), which together capture 43.3% of the total variance in the volatile compound data. The samples are distributed across all four quadrants, indicating a wide range of volatile compositions. However, the lack of distinct clustering suggests that some samples share more similarities than differences in their volatile profiles.

- Volatiles distribution

(a) Aldehyde and Ester

Elation and Viscount from the location Carlow and Torp from Tipperary, from the year 2020, had a higher concentration of aldehydes (straight chain, branched chain, and aromatic) and esters. These compounds are known to contribute to the fruity, floral, and sometimes nutty flavour of whiskey. In comparison, a group of samples from 2021-LG Astronomer, Torp, Viscount from Carlow, LG Astronomer, and Torp from Tipperary had a higher abundance of mainly aldehydes and a very low abundance of esters. Elation Tipperary 2021, Viscount Tipperary 2021, Revelation Carlow 2021, and LG Astronomer Carlow 2020, Revelation Carlow 2020, Revelation Tipperary 2020, and Torp Tipperary 2020 located on the negative side of the PC-1 plot were characterised by a low abundance of aldehydes and have a high abundance of specific esters.

(b) Acetals and Alcohol Ester

There is one more cluster of samples mainly associated with acetals and alcohols, especially ethanol and phenyl ethyl alcohol at the bottom right corner of the PCA (Elation Tipperary 2020, Elation Carlow 2021, LG Astronomer Tipperary 2021, LG Astronomer Carlow 2021, Viscount Tipperary 2020, Viscount Carlow 2021, Torp Carlow 2021, Torp Tipperary 2021, and Revelation Tipperary 2021). The 2021 samples had a higher abundance of these volatiles compared to the 2020 samples.

Total peak Area Variability: The peak areas also varied considerably across sample sets. Torp Tipperary 2020 and Viscount Tipperary had the largest peak area, whereas Viscount Carlow 2020 and LG Astronomer Tipperary 2021 had the lowest peak area. Having larger peak areas suggests richer or more intensive flavour profiles, possibly due to the region's specific conditions in that year.

Further analysis, which separated the samples based on a single factor such as year and location, as shown in Figures 2 and 3, highlighted that year and location had more impact on the volatiles compared to the variety. Figure 2 highlights the impact of the harvest year on the volatile profiles. The red (2020) and blue (2021) ellipses show a distinct separation, indicating that the harvest year significantly influenced the volatile composition of the newly made spirit. These results can be attributed to the differences in growing conditions between 2020 and 2021, such as variations in temperature and rainfall, which influenced the grain composition and, ultimately, the volatile profile of whiskey. Figure 3 shows the influence of location (Carlow vs. Tipperary) on the volatile profile. The samples from Carlow (red) are more dispersed compared to those from Tipperary (blue), suggesting greater variability in the environmental conditions in Carlow, potentially due to its heterogeneous soil types and microclimate. In contrast, the more uniform conditions in Tipperary may have contributed to a narrower range of volatile profiles.

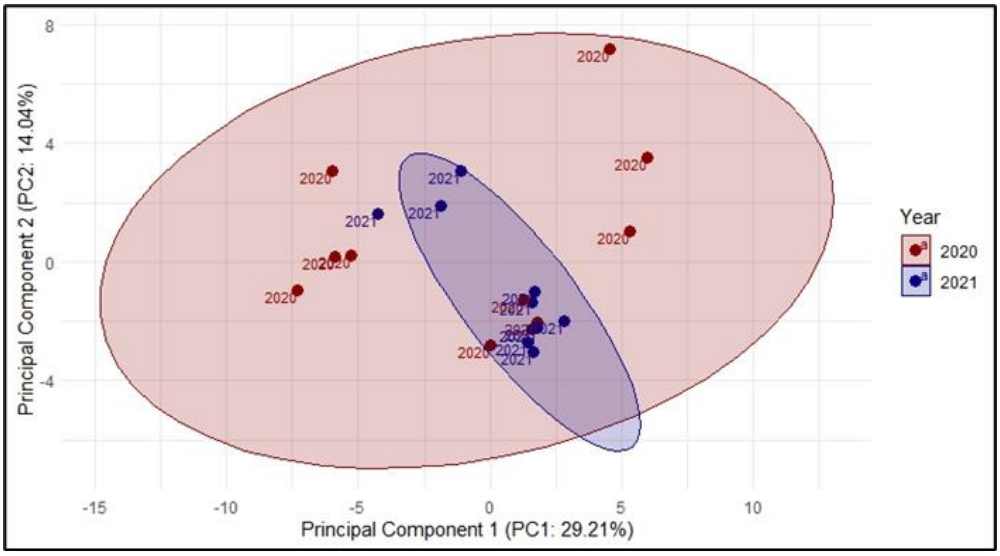

Figure 2. PCA plot and groups of spirit according to harvest year (2020 and 2021).

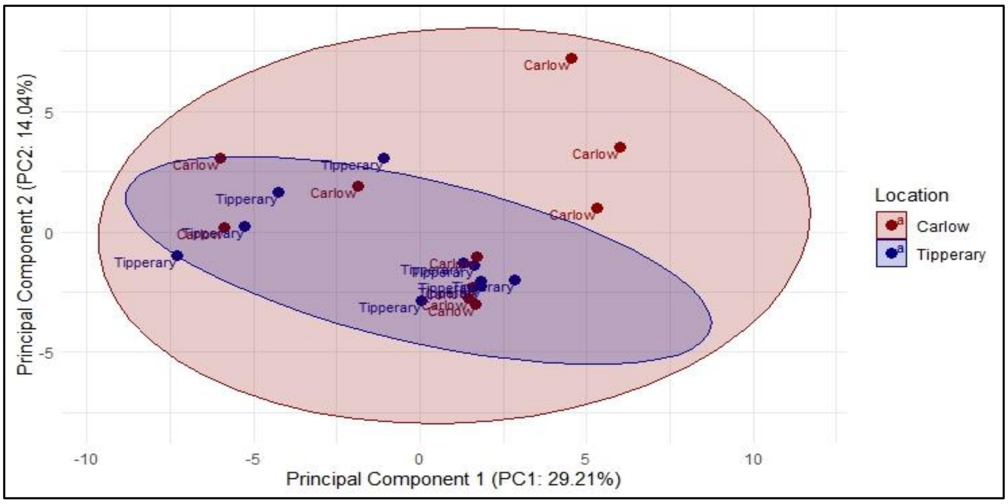

Figure 3. PCA plot and groups of spirits according to location (Carlow and Tipperary).

4. Conclusions

This study provides valuable insights into the influence of terroir factors on the grain composition and volatile profile of the wheat-based newly made spirit, highlighting the relevance of environmental factors such as season, geography, and variety in spirit production.

- Influence of Terroir on grain composition:

The grain composition was significantly affected by the variety, year, and location where the grains were grown. Understanding the effect of these factors is crucial, as grain composition not only affects the processing characteristics (such as mashing and fermentation efficiency) but also ultimately influences the flavour perception of the final whiskey. Key findings include the following:

1. The harvest year (vintage effect) significantly impacted the protein, starch, β-glucan, and arabinoxylan contents. The 2020 samples exhibited higher protein and β-glucan content compared to 2021, likely due to favourable climatic conditions such as rainfall and temperature. However, caution needs to be taken as a high β-glucan content in grain can also result in processability issues due to increased viscosity.

2. Location (Tipperary vs. Carlow): The location of wheat cultivation significantly influenced its starch, β-glucan, and arabinoxylan content. Tipperary showed consistently higher starch content compared to Carlow, likely due to its nutrient-rich, loamy soils. The higher starch content supports greater sugar availability during mashing, favouring the production of esters, which impart fruity and floral notes. In contrast, arabinoxylans and β-glucan can influence viscosity and affect fermentation kinetics, ultimately contributing to flavour complexity.
3. Variety: The variety of wheat plays an essential role in defining the starch, protein, and non-starch polysaccharide content. Torp and Revelation varieties had higher protein content, which enhances yeast activity and results in increased fusel alcohol production. Viscount, with its higher starch content, contributes more to a light and fruity character, and increased alcohol content. Understanding these varietal effects allows distillers to control grain characteristics that ultimately affect the flavour development and mouthfeel of the whiskey.
4. The interaction effect of variety x location x year significantly affected the non-starch polysaccharide content.

- Influence of Terroir on Volatile Distribution:
    1. The result illustrates a clear separation between the 2020 and 2021 samples, with the year contributing to the distinct volatile profiles. This difference aligns with the variation in environmental conditions such as rainfall and temperature; the 2020 season was warmer compared to 2021, affecting the grain composition and volatile formation.
    2. The PCA plot by location shows greater dispersion in Carlow samples compared to Tipperary, suggesting more variable environmental conditions, potentially due to its heterogeneous soil types and microclimate. In contrast, Tipperary's more uniform soil and climate conditions contribute to a narrower range of volatiles.
    3. The wheat spirit was characterised by a wide range of volatile compounds, but the overall variability in the volatile profile was relatively low compared to the malt whiskey profile, as during the malting process, barley undergoes enzymatic changes that lead to the development of numerous flavour compounds [9].

The above findings suggest that wheat may be a less complex contributor to the aroma and flavour of the whiskey, aligning with its role as a "diluent" in blended whiskeys. This simplicity could be advantageous in blends where the desired flavour profile comes primarily from malt or pot still whiskey, allowing for the wheat to contribute to a smooth, neutral base without overpowering the palate with strong flavours [28].

Understanding this can be of importance to tillage farmers and distillers regarding the selection of wheat varieties and cultivation sites to optimise the production of high-quality Irish whiskey. The study also reinforces the applicability of the terroir concept beyond viticulture, extending it to the production of distilled spirits, particularly grain-based Irish whiskey. It also aligns with the growing consumer interest in authenticity and locality in food and beverage products.

Future Research Directions: To better understand the specific contributions of individual terroir components, future studies should aim to isolate variables such as soil type, temperature, or nutrient availability and conduct controlled experiments. This would help to more precisely quantify the influence of each factor on the whiskey's aromatic and sensory profile. Moreover, expanding the analysis to include sensory evaluation alongside chemical profiling could provide further insight into how terroir affects the consumer perception of whiskey, thereby linking chemical composition to consumer preference and marketability.

In summary, while terroir influences wheat-based whiskey production, its impact is quite subtle. Nevertheless, these findings highlight an important opportunity for the Irish whiskey sector to differentiate its products by leveraging local environmental factors, particularly as consumer preferences continue to shift towards sustainability and locality.

Author Contributions: Conceptualisation, A.V. and S.M.; methodology, A.V. and S.M.; validation, A.V., K.N.K., I.S., J.L.B. and S.M.; formal analysis, S.M. and A.V.; data curation, A.V., S.M. and K.N.K.; writing—original draft preparation, A.V.; writing—review and editing, A.V., S.M., S.W., J.L.B., G.G.-C. and K.N.K.; supervision, S.M., S.W., J.L.B. and G.G.-C. All authors have read and agreed to the published version of the manuscript.

Funding: The research is funded by President's fellowship awards, South East Technological University, Carlow, under account PES3821.

Data Availability Statement: The authors confirm that the data supporting the findings of this study are available within the article.

Conflicts of Interest: The authors declare no conflicts of interest.

Appendix A

Table A1. IDs and plot codes of the samples analysed.

S.No.	Table and Plot Codes	Sample ID	ABV%
1	Rev Carl '21	Revelation Carlow 2021	5
2	Rev Tipp '21	Revelation Tipperary 2021	8
3	Rev Tipp '20	Revelation Tipperary 2020	4
4	Rev Carl '20	Revelation Carlow 2020	6
5	Vis Tipp '20	Viscount Tipperary 2020	5
6	Vis Tipp '21	Viscount Tipperary 2021	5
7	Vis Carl '20	Viscount Carlow 2020	3
8	Vis Carl '21	Viscount Carlow 2021	4
9	Ela Carl '20	Elation Carlow 2020	6
10	Ela Carl '21	Elation Carlow 2021	8
11	Ela Tipp '20	Elation Tipperary 2020	8
12	Ela Tipp '21	Elation Tipperary 2021	4
13	Ast Carl '20	LG Astronomer Carlow 2020	5
14	Ast Carl '21	LG Astronomer Carlow 2021	7
15	Ast Tipp '20	LG Astronomer Tipperary 2020	3
16	Ast Tipp '21	LG Astronomer Tipperary 2021	5
17	Torp Tipp '20	Torp Tipperary 2020	5
18	Torp Tipp '21	Torp Tipperary 2021	5
19	Torp KB '20	Torp Carlow 2020	5
20	Torp KB '21	Torp Carlow 2021	5

Table A2. Grain composition (protein, starch, arabinoxylans, and β-glucans for 4 different wheat varieties grown at two different sites and harvested in two different years, all readings were recorded in triplicate and presented as their average ± standard deviation.

Variety	Year	Location	Protein ± SD	Starch ± SD	Arabinoxylans ± SD	β-glucan ± SD
Elation	2020	Tipperary	9.82 ± 0.44	77.07 ± 3.76	6.172 ± 1.42	3.16 ± 0.2
Elation	2020	Carlow	10.06 ± 0.11	62.44 ± 0.12	3.86 ± 0.45	7.12 ± 1.45
Elation	2021	Tipperary	8.38 ± 0.22	74.04 ± 3.72	0.23 ± 0.05	4.97 ± 0.92
Elation	2021	Carlow	7.64 ± 0.22	73.76 ± 2.03	16.42 ± 2.46	7.69 ± 1.04
LG Astronomer	2020	Tipperary	9.83 ± 0.21	85.90 ± 1.87	11.097 ± 2.56	4.97 ± 2.48
LG Astronomer	2020	Carlow	10.36 ± 0.28	70.58 ± 1.20	15.94 ± 1.88	5.22 ± 0.65
LG Astronomer	2021	Tipperary	8.76 ± 0.4	73.82 ± 5.07	15.85 ± 3.71	3.15 ± 0.57
LG Astronomer	2021	Carlow	8.31 ± 0.22	54.25 ± 0.69	9.25 ± 1.3	7.85 ± 1.04
Revelation	2020	Tipperary	10.23 ± 0.39	81.53 ± 7.67	11.166 ± 2.56	2.97 ± 0.15
Revelation	2020	Carlow	10.07 ± 0.24	69.17 ± 3.05	15.7 ± 1.83	5.62 ± 1.03
Revelation	2021	Tipperary	8.69 ± 0.18	89.18 ± 1.96	10.91 ± 2.56	2.2 ± 0.08
Revelation	2021	Carlow	8.5 ± 0.34	63.08 ± 10.54	12.08 ± 2.84	4.84 ± 0.62
Torp	2020	Tipperary	10.31 ± 0.36	77.76 ± 1.6	15.811 ± 3.63	3.4 ± 0.33
Torp	2020	Carlow	11.78 ± 0.09	73.65 ± 8.29	10.11 ± 0.77	10.05 ± 0.83
Torp	2021	Tipperary	8.8 ± 0.45	82.55 ± 21.75	10.15 ± 2.39	3.9 ± 0.05
Torp	2021	Carlow	8.64 ± 0.21	68.61 ± 3.46	16.76 ± 2.11	3.7 ± 0.15
Viscount	2020	Tipperary	10.024 ± 0.48	88.279 ± 2.14	15.32 ± 3.51	5.98 ± 1.1
Viscount	2021	Carlow	10.35 ± 0.32	75.86 ± 2.044	11.34 ± 0.72	7.51 ± 2.3
Viscount	2021	Tipperary	8.44 ± 0.26	91.89 ± 1.97	12.01 ± 2.81	3.79 ± 0.28
Viscount	2021	Carlow	7.79 ± 0.13	63.89 ± 41.09	14.39 ± 3.61	3.85 ± 0.77

Table A3. Compounds identified by HS-SPME GCMS in the New- Make spiritsamples.

Name	CAS	RI	Ref RI	Rev Carl '21	Rev Tipp '21	Rev Tipp '20	Rev Carl '20	Vis Tipp '20	Vis Tipp '21	Vis Carl '20	Vis Carl '21	Ela Carl '20	Ela Carl '21
Acetal													
Diethyl acetal	105-57-7	742	747	0	30,871	0	0	0	0	0	0	0	28,584
3-Methylbutanal, diethyl acetal	03-03-3842	960	*	0	4581	0	0	0	0	2507	0	2453	5855
Alcohol													
Ethanol	64-17-5	489	506	3,658,448	5,926,241	2,089,463	2,570,413	1,870,733	3,232,613	3,2867,58	2,136,321	1,996,144	7,608,948
1-Propanol, 2-methyl-	78-83-1	673	678	74,491	139,037	103,936	103,228	85,015	77,912	124,427	53,882	112,148	126,817
1-Butanol, 3-methyl-	123-51-3	779	784	1,579,432	2,367,820	1,063,291	1,169,229	1,147,384	1,275,580	1,119,081	1,219,898	1,510,003	1,965,940
1-Butanol, 2-methyl-	137-32-6	782	789	887,119	1,288,811	868,408	937,931	929,593	757,457	751,201	683,873	973,218	1,193,111
1-Hexanol	111-27-3	911	915	77,158	102,252	88,872	96,213	93,247	105,157	90,652	64,701	122,381	63,404
2-Heptanol	543-49-7	938	947	0	0	20,480	20,626	0	0	0	0	0	0
1-Heptanol	111-70-6	1011	1016	7241	6211	6772	7187	4754	7153	5771	2940	6842	0
2-Octanol, (S)	08-06-6169	1032	*	0	0	0	0	3042	0	0	0	0	0
1-Octanol	111-87-5	1112	1118	6704	7362	6242	5738	7183	7256	14,204	7239	14,528	7484
2-Nonanol	628-99-9	1136	1143	0	0	0	0	0	0	0	0	0	0
Phenylethyl Alcohol	60-12-8	1194	1201	1,320,950	1,588,485	1,603,174	1,430,394	1,842,483	1,354,686	941,109	1,080,744	1,226,542	2,278,321
2-Furanmethanol	98-00-0	924	*	4180	0	8398	9722	0	3163	0	0	0	0
Aldehyde													
Butanal, 3-methyl-	590-86-3	687	692	5285	14,163	6824	11,337	36,088	5969	29,434	18,860	39,224	16,673
Butanal, 2-methyl-	96-17-3	695	700	23,714	4951	5761	7115	18,954	4706	14,973	10,322	16,807	10,211
Hexanal	66-25-1	834	839	0	8433	0	0	19,255	0	32,237	16,804	38,371	9770
Furfural	98-01-1	894	899	0	12,769	0	0	73,454	0	366,244	81,629	261,486	31,537
Heptanal	111-71-7	936	943	0	0	0	0	2805	0	4694	2637	3916	0
Benzaldehyde	100-52-7	1024	1031	0	2173	0	0	6426	0	43,866	12,277	28,300	3051
Benzenacetaldehyde	122-78-1	1114	*	0	4305	0	0	25,416	0	279,059	2585	108,461	18,543
Nonanal	124-19-6	1143	1150	3448	9734	2385	1370	6796	772	13,537	14,016	6980	8872
Benzaldehyde, 4-propyl-	28785-06-0	1357	*	0	18,739	4338	6002	23,560	3689	17,438	17,509	10,527	14,337
Benzene													
Styrene	100-42-5	923	929	0	0	0	0	0	0	0	0	0	0
o-Xylene	108-38-3	922	929	5084	3676	4291	5052	7449	4622	5330	3605	0	0
Ester													
Ethyl acetate	141-78-6	636	642	3,285,572	265,629	6,266,471	6,384,798	235,939	7,142,368	103,024	147,009	252,082	544,533
Ethyl propanoate	105-37-3	732	737	14,319	0	31,339	40,564	10,547	28,353	0	4230	12,874	9020
n-Propyl acetate	109-60-4	738		0	0	7563	20,808	0	17,335	0	0	0	0
Isobutyl acetate	110-19-0	795	800	0	0	0	0	0	0	0	0	0	0
Ethyl butanoate	105-54-4	820	826	5402	4974	4399	4945	7823	4521	0	3166	6464	7613
Isoamyl acetate	123-92-2	898	902	320,930	75,612	411,020	464,540	121,647	518,464	75,832	82,041	205,476	115,743
2-Methylbutyl acetate	624-41-9	901	906	108,183	0	182,515	201,899	54,666	173,550	18,491	0	77,946	115,595
Ethyl pentanoate	539-82-2	920	924	2414	3737	2684	0	5392	8063	3790	2651	10,624	4030
Isopropyl pentanoate	18362-97-5	957	*	4603	3246	5769	5439	8164	4947	4323	4423	7377	2101
Ethyl hexanoate	123-66-0	1017	1024	193,226	140,281	82,842	62,344	142,815	285,002	141,487	116,807	611,323	173,458
Hexyl acetate	142-92-7	1034	*	24,461	0	40,009	38,010	0	62,198	0	0	0	0
Ethyl heptanoate	106-30-9	1115	*	5185	2417	2440	9399	1928	6243	2427	1804	20,061	4262
Ethyl octanoate	106-32-1	1216	1222	115,602	4251	2955	0	3102	20,604	5364	8243	102,467	60,572
Ethyl benzoate	93-89-0	1225	1232	1636	1648	0	0	0	0	1938	0	3867	2176

Table A3. *Cont.*

Name	CAS	RI	Ref RI	Rev Carl '21	Rev Tipp '21	Rev Tipp '20	Rev Carl '20	Vis Tipp '20	Vis Tipp '21	Vis Carl '20	Vis Carl '21	Ela Carl '20	Ela Carl '21
Octyl acetate	112-14-1	1215	*	0	0	0	0	0	0	10,159	4470	0	0
B-Phenylethyl acetate	103-45-7	1313	1322	40,527	12,721	73,283	69,985	8259	77,165	20,195	21,820	16,808	22,582
Ethyl nonanoate	123-29-5	1314	*	4470	0	1651	0	0	2519	0	0	1710	0
Ethyl decanoate	110-38-3	1414	1422	5072	0	0	0	0	0	0	2012	10,031	3325
Ethyl benzeneacetate	101-97-3	1298	*	10,189	14,785	0	0	1767	2412	6214	0	3793	18,290
Ether													
Difurfuryl ether	4437-22-3	926	*	0	0	0	0	0	0	4023	0	0	0
Furan													
Furfuryl acetate	623-17-6	1030	*	0	0	3377	3303	0	1358	0	0	0	0
Ketone													
2-Heptanone	110-43-0	930	936	24,503	0	133,423	127,576	12,130	9350	12,933	7078	10,681	0
3-Octanone	106-68-3	1022	*	0	0	0	0	0	0	0	0	0	0
4-Nonanone, 2,6,8-trimethyl-	123-18-2	1247	*	3942	4874	5234	4072	4654	5058	4151	3839	5206	4817
Lactone													
γ-Nonalactone	104-61-0	1484	*	31,873	52,879	22,125	18,433	28,241	64,719	51,897	25,520	61,895	46,106
Phenol													
2,4-Di-tert-butylphenol	96-76-4	1592	1644	33,250	36,216	33,091	30,931	35,051	38,713	29,773	20,547	61,121	34,506

Compound identification, chemical class, and average abundance values measured (n = 3); CAS: chemical CAS (chemical abstract service) (blanks relate to isomers where we could not be 100% sure of identification and therefore could not provide full identification. LRI: linear retention indices as determined using the method by Van Den Dool and Kratz (1963); REF LRI: These values were obtained from published papers or NIST 2014. *: No published reference available to date (not many published as yet on a DB624 column), tentative identification, might be isomer of this chemical compound.

Table A4. Compounds identified by HS-SPME GCMS in the New-Make spiritsamples.

Name	CAS	RI	Ref RI	Ela Tipp '20	Ela Tipp '21	Ast Carl '20	Ast Carl '21	Ast Tipp '20	Ast Tipp '21	Torp Tipp '20	Torp Tipp '21	Torp KB '20	Torp KB '21
Acetal													
Diethyl acetal	105-57-7	742	747	0	0	0	0	0	0	0	0	0	0
3-Methylbutanal, diethyl acetal	03-03-3842	960	*	4985	0	0	2719	0	0	0	2437	2441	0
Alcohol													
Ethanol	64-17-5	489	506	5,257,459	2,715,097	1,970,918	4,789,790	3,056,767	2,330,556	2,532,878	3,514,650	2,738,950	3,216,485
1-Propanol, 2-methyl-	78-83-1	673	678	69,527	113,733	107,524	80,899	81,212	59,137	101,917	89,568	142,289	76,400
1-Butanol, 3-methyl-	123-51-3	779	784	1,262,577	1,032,851	1,622,604	1,514,584	952,109	1,239,367	1,112,751	1,792,022	1,134,854	1,221,304
1-Butanol, 2-methyl-	137-32-6	782	789	669,247	57,3149	889,173	908,836	779,533	693,110	946,563	872,999	740,315	642,925
1-Hexanol	111-27-3	911	915	78,012	78,875	161,625	74,317	76,276	75,196	62,859	91,487	86,675	54,189
2-Heptanol	543-49-7	938	947	0	0	152,703	0	0	0	0	0	0	0
1-Heptanol	111-70-6	1011	1016	5164	4483	19,280	7970	5433	0	6165	3730	3766	0
2-Octanol, (S)	08-06-6169	1032	*	0	0	12,432	0	0	0	0	0	0	0
1-Octanol	111-87-5	1112	1118	5764	4588	6748	6375	4019	8275	4588	8849	15,465	6091
2-Nonanol	628-99-9	1136	1143	0	0	249,369	0	0	0	0	0	0	0

Table A4. *Cont.*

Name	CAS	RI	Ref RI	Ela Tipp '20	Ela Tipp '21	Ast Carl '20	Ast Carl '21	Ast Tipp '20	Ast Tipp '21	Torp Tipp '20	Torp Tipp '21	Torp KB '20	Torp KB '21
Phenylethyl Alcohol	60-12-8	1194	1201	1,543,105	868,736	969,069	1,597,147	1,325,589	1,336,868	1,560,983	2,055,401	847,927	1,446,128
2-Furanmethanol	98-00-0	924	*	0	0	11,720	0	0	0	3496	0	0	0
						Aldehyde							
Butanal, 3-methyl-	590-86-3	687	692	14,080	2615	2705	22,557	21,961	21,800	0	23,375	33,697	20,258
Butanal, 2-methyl-	96-17-3	695	700	5962	6438	5845	9985	7644	7890	0	0	18,058	9378
Hexanal	66-25-1	834	839	9945	0	0	7481	0	18,822	0	20,502	40,568	17,604
Furfural	98-01-1	894	899	78,683	29,958	0	253,996	86,332	91,317	0	367,941	345,793	183,414
Heptanal	111-71-7	936	943	2142	0	0	2707	0	3592	0	3977	7005	2489
Benzaldehyde	100-52-7	1024	1031	4457	7481	0	21,626	7158	14,468	0	28,580	48,370	13,763
Benzenacetaldehyde	122-78-1	1114	*	28,305	1730	0	22,275	2557	0	0	30,919	214,466	26,191
Nonanal	124-19-6	1143	1150	8963	1569	0	6690	7273	13,796	992	22,463	16,959	15,245
Benzaldehyde, 4-propyl-	28785-06-0	1357	*	17,233	5843	0	22,308	16,027	19,601	0	25,444	18,691	20,997
						Benzene							
Styrene	100-42-5	923	929	0	10,184	0	0	0	0	2299	0	1097	1222
o-Xylene	108-38-3	922	929	2443	0	7250	6023	6233	4349	5714	5984	4769	6240
						Ester							
Ethyl acetate	141-78-6	636	642	196,102	2,593,055	2,150,842	225,220	175,361	165,889	7,520,894	425,306	141,353	221,336
Ethyl propanoate	105-37-3	732	737	0	39,820	22,481	5393	13,938	6314	45,558	0	0	0
n-Propyl acetate	109-60-4	738		0	0	0	0	0	0	38,102	0	0	0
Isobutyl acetate	110-19-0	795	800	0	0	35,914	0	0	0	37,543	0	0	0
Ethyl butanoate	105-54-4	820	826	2978	1117	5188	4538	5253	4665	5082	4245	885	4442
Isoamyl acetate	123-92-2	898	902	40,886	237,443	433,820	92,222	92,689	104,991	644,723	134,687	105,384	117,554
2-Methylbutyl acetate	624-41-9	901	906	27,674	64,857	151,657	91,890	68,706	100,866	305,136	132,971	45,609	116,627
Ethyl pentanoate	539-82-2	920	924	4076	7055	2462	1397	4025	3380	0	3630	3975	2148
Isopropyl pentanoate	18362-97-5	957	*	2171	4833	7043	6145	5798	5562	6000	5459	5364	5906
Ethyl hexanoate	123-66-0	1017	1024	121,759	302,117	60,166	79,233	90,102	159,323	22,728	114,735	196,110	64,722
Hexyl acetate	142-92-7	1034	*	0	24,781	24,106	0	0	0	35,690	0	0	0
Ethyl heptanoate	106-30-9	1115	*	2851	9359	0	0	0	2935	0	1921	11,153	0
Ethyl octanoate	106-32-1	1216	1222	11,834	28,235	1463	5590	2409	13,317	0	5475	61,218	3130
Ethyl benzoate	93-89-0	1225	1232	520	1270	3160	0	0	0	0	0	2254	0
Octyl acetate	112-14-1	1215	*	0	0	0	0	0	9045	0	0	0	4501
B-Phenylethyl acetate	103-45-7	1313	1322	14,485	33,770	21,010	16,997	6091	24,876	91,152	15,647	19,622	17,318
Ethyl nonanoate	123-29-5	1314	*	0	4403	2340	0	0	0	0	0	0	0
Ethyl decanoate	110-38-3	1414	1422	0	7139	0	0	0	0	0	0	5250	0
Ethyl benzeneacetate	101-97-3	1298	*	13,088	6780	0	0	0	0	0	0	8167	0
						Ether							
Difurfuryl ether	4437-22-3	926	*	0	0	0	0	0	0	0	0	3294	0

Table A4. *Cont.*

Name	CAS	RI	Ref RI	Ela Tipp '20	Ela Tipp '21	Ast Carl '20	Ast Carl '21	Ast Tipp '20	Ast Tipp '21	Torp Tipp '20	Torp Tipp '21	Torp KB '20	Torp KB '21
Furan													
Furfuryl acetate	623-17-6	1030	*	0	0	1317	0	0	0	2157	0	0	0
Ketone													
2-Heptanone	110-43-0	930	936	0	21,446	35,054	9131	12,311	7900	22,187	8363	78,087	8480
3-Octanone	106-68-3	1022	*	0	0	0	10,084	8369	0	0	0	0	0
4-Nonanone, 2,6,8-trimethyl-	123-18-2	1247	*	4114	4229	4253	5490	4449	4719	4049	5298	5124	5212
Lactone													
γ-Nonalactone	104-61-0	1484	*	80,355	94,137	22,099	32,877	23,637	34,166	16,892	65,773	64,032	30,489
Phenol													
2,4-Di-tert-butylphenol	96-76-4	1592	1644	23,969	19,170	28,656	39,295	28,938	25,377	34,329	40,321	38,226	29,813

Compound identification, chemical class, and average abundance values measured (n = 3); CAS: chemical CAS (chemical abstract service) (blanks relate to isomers where we could not be 100% sure of identification and therefore could not provide full identification. LRI: linear retention indices as determined using the method by Van Den Dool and Kratz (1963). REF LRI: These values were obtained from published papers or NIST 2014. *: No published reference available to date (not many published as yet on a DB624 column), tentative identification, might be isomer of this chemical compound.

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