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Tracking dry gin volatile organic compounds over distillation: a time course study

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Abstract

Why was the work done: The influence of distillation time on the volatile composition of gin has not been examined in detail at a commercial distillery.
How was the work done: Headspace Solid-Phase Micro-Extraction Gas Chromatography-Mass Spectrometry (HS-SPME-GC-MS) was used to tentatively identify 74 aroma compounds, with their concentration tracked in distillate samples over the course of three gin distillations.
What are the main findings: Four unique fractions were identified using Agglomerative Hierarchical Clustering: 'heads', 'early hearts', 'late hearts, and 'tails'. The hearts fraction (n=24 samples) was examined further, fitting statistically appropriate models to 54 aroma volatiles. Three sub-groups of volatiles were identified, (i) highly volatile monoterpenes with rapidly decreasing concentration over the early hearts fraction, (ii) volatiles whose concentration increased gradually over the hearts fraction and (iii) less volatile sesquiterpenes, sesquiterpenoids, and monoterpenoids which increased rapidly in concentration in the later distillate. Complex cubic models fit 34 volatiles with very high significance ($p>0.0001$) over the hearts fraction (72%). Informal aroma sensory bench testing identified distinct aroma categories with, for example, 'Spicy' being commonly detected in the later distillate.
Why is the work important: This investigation characterises the kinetics of flavour extraction over the course of a commercial gin distillation process. These findings highlight the potential for the expression of specific flavour characteristics by modifying the cut points of the distillation process.

Keywords:

Gin, distillation, flavour, modelling flavour release, terpenes, headspace solid-phase micro-extraction gas chromatography-mass spectrometry (HS-SPME-GC-MS), volatile organic compounds.

Introduction

Gin, a juniper flavoured spirit drink, is said to originate in the Netherlands in 1650 as ‘genever’ (Greer et al. 2008). Intended as a method of orally administering juniper oil, Dutch physician and Professor Franciscus de la Boë used neutral grain spirits and fruit brandies enriched with juniper essential oil to treat patients with kidney disorders (Clutton and Evans 1978; Greer et al. 2008). The use of juniper berries in drinks can be traced back even further in Dutch literature to 1266 (Hodel et al. 2019).

The reputation of gin has evolved over the centuries. Firstly, as a continental medicinal spirit (‘genever’), which was discovered by English soldiers as the ‘Dutch courage’ which Dutch soldiers would drink before battle. This was later anglicised to ‘gin’, where consumption increased rapidly by the poorer members of society in England in the 18th century, leading to the colloquial names: ‘Madame Genever’ and ‘Mother’s ruin’ (Pedeliento et al. 2022). In the 19th century, the status of gin became more respectable as quality improved, while British colonialists globalised gin consumption. Throughout the 20th century, the popularity of gin fluctuated, and for the first time in 1967, sales of vodka exceeded those of gin (Pedeliento et al. 2022). However, gin has experienced a revival in recent decades, where the market has undergone worldwide expansion. For example, in 2019 there were 225 gin brands in Italy with gin distillers all but non-existent before the early 2000s (Pedeliento et al. 2022). Similarly, the number of gin distilleries in the UK tripled to 360 between 2012 and 2019 (Pedeliento et al. 2022).

Consumer acceptance of beverages is driven primarily by flavour (Buck et al. 2020). The resurgence of the popularity of gin is due, in part, to the wide range of available flavour profiles. Gin is flavoured with botanicals, which impart their flavour volatiles into the ethanol spirit. EU legislation limits gin flavourings to being natural or nature-identical, also stipulating that the prevalent flavour must be that of juniper (*Juniperus communis* L.) (EU 2008). However, the array of botanicals is not limited by legislation. Gin distillers may blend different botanicals to achieve the desired flavour profile. This is commonly achieved by those skilled in the art. In addition to juniper berries, commonly included botanicals include coriander seed, angelica root, orange peel, lemon peel, orris root, liquorice root, cardamom, cinnamon, and cassia bark.

Variation may also be introduced by the method of distillation. There are three major categories of gin production: distilled gin, London (dry) gin, and compound gin. Distilled gin must contain neutral ethanol (of agricultural origin and appropriate organoleptic quality at >96% ABV) redistilled with (or through) botanicals, which post distillation can be flavoured by natural or nature-identical flavourings (Willkie 1937; EU 2008). London gin is distilled gin, where flavour and colour is achieved by re-distillation only. The sugar content must not exceed 0.1 g/L (EU 2008) and is accordingly ‘dry’. Compound gin is produced by adding essences or flavourings to ethanol of appropriate quality without redistillation. All gin must be bottled to at least 37.5% ABV (EU 2008).

In gin distillation, flavour volatiles from botanicals are extracted into a mixture of grain neutral spirit (GNS) and water, which vaporises, undergoes reflux (the extent of which depends upon the still design) and condenses to a liquid. The objective of gin distillation is to extract desirable flavour, while minimising excessive flavour volatile extraction from the botanical ingredients (Hodel et al. 2020). Spirit distillation is split into three major fractions: the ‘heads’, ‘hearts’, and ‘tails’. The first fraction the 'heads', contains the most volatile compounds that elute from the still of which some can be undesired (e.g. methanol). The second fraction the 'hearts', forms the final spirit and contains desirable volatile compounds. The final fraction the 'tails', contains the least volatile compounds which have negative organoleptic qualities. This fraction also contains compounds which may have formed during the distillation process (Rodríguez-Bencomo et al. 2016).

The volatile composition of gin is influenced by the inclusion of botanicals (Clutton and Evans 1978). Additionally, for cardamom, black pepper, elderflower, cinnamon and cassia bark, the geographical origin and botanical variety is known to influence the volatile composition of botanicals (Jayatilaka et al. 1995; Jagella and Grosch 1999; Joshi et al. 2013; Pabl et al. 2014; Baby and Ranganathan

2016). For example, angelica root may or may not contain 3-carene depending on its geographical origin (Holm et al. 1997). The concentration of volatiles also reflects processing variables such as the spirit raw material, still type (column, pot, or hybrid), still material (copper, stainless steel, or glass), distillation atmospheric pressure (vacuum distillation), extent of reflux, botanical infusion (vapour infused or steeped), and length of maceration (Willkie 1937; Greer et al. 2008; Rodríguez-Bencomo et al. 2016; Hodel et al. 2019; Hodel et al. 2020; Hodel et al. 2021). For example, Greer et al (2008) reported that excess heat should be avoided when distilling 'super premium' gins to reduce off-flavours and maintain the natural flavour profile of the botanicals. Hodel et al (2019) reported that vapour infused gins have a lighter flavour due to the reduced thermal influence on botanicals, but contain more monoterpenes than steep infusion. Hodel et al (2020) also found that the ratio of botanicals influenced the volatile composition of gin, above the influence of ethanol concentration. Accordingly, the variables that can be used to influence the flavour profile of a gin is vast.

Legally, as every gin must contain the flavour of juniper (either by redistillation or addition of juniper oil/essence), gins will always share flavour characteristics. Vichi et al (2007) identified 77 volatile compounds in juniper berries by headspace solid-phase micro-extraction (HS-SPME) gas chromatography mass spectrometry (GC-MS). More than 70% of the volatile composition of juniper was identified to be terpinene-4-ol, p-cymene, myrcene, g-terpinene, a-pinene, and limonene. Most of the identified compounds in juniper were monoterpenic or sesquiterpenic. Terpenes are aromatic hydrocarbons with the general formula $(C_5H_8)_n$ (Hancı et al. 2003). Monoterpenes and sesquiterpenes are sub-categories of the wider terpene category, where n=2 and n=3, respectively. Terpenoids are chemically modified terpenes, typically oxygenated derivatives which include alcohols, ketones, aldehydes, carboxylic acids, and esters (Bruneau et al. 2018).

Investigations into the flavour and aroma activity of gin volatiles have been invaluable in providing insight to distillation and flavour. Clutton and Evans (1978) compared the volatile analysis of gin with those of steam distilled juniper berry and coriander seed essential oils, identifying the source of key flavour volatiles. Riu-Aumatell et al (2008) discriminated the volatile composition of six dry gins to their sensory characterisation using five attributes: juniper, citric, aniseed, liquorice, and spice. Further, an investigation into the differences between high vacuum and conventional gin distillation methods found that the novel (high vacuum) method reduced the number and concentration of monoterpenes (Greer et al. 2008). In the same study, it was noted that the inclusion of juniper influenced the volatile contribution of additional botanicals, suggesting some interaction between volatiles in the still. Hodel et al (2020) investigated the influence of distillation parameters on the extraction of nine common flavour volatiles in vapour infused gin, identifying the botanical ratio as the most influential factor. In chemosensory analysis, Dussort et al (2012) used GC-Olfactometry (GC-O) to identify 38 odour active compounds from two gin samples (London dry and distilled), with the majority of identified compounds being terpenoids. In addition, Buck et al (2020) identified 38 odour active compounds in two Bavarian gins (one containing 50 botanicals, and the other containing 15), where 18 of the identified compounds were reported for the first time.

Only a few investigations of the time course of flavour volatiles during distillation have been reported. The majority of these studies investigate essential oil distillation, which relies upon steam distillation or hydrodistillation in the absence of ethanol (Hodel et al. 2020). Markovic et al (2017) described the juniper essential oil yield over time from two distillation methods (hydrodistillation, and simultaneous hydrodistillation and rectification), tracking the flavour volatile composition of the fractions obtained during distillation. Cassel et al (2009) reported the time course of steam distillation, modelling the extraction curves of three herb essential oils which followed the same behaviour in all three systems, but the authors did not report the concentration of volatiles over distillation.

More recently, Hodel et al (2021) investigated the influence of key distillation parameters on ten common volatile terpenes in an artificial model gin over four distillate fractions. It was found that monoterpenes were the most volatile compound group, oxygenated terpenes increased in concentration with depleting ethanol concentration, and sesquiterpenes were found to be semi-volatile.

The current study models the release of flavour volatiles in a commercial-scale gin distillation process. An understanding of the emission of flavour volatiles through distillation will provide gin distillers with insight to tailor distillate flavour further to express target characteristics. This investigation describes the release of aromatic volatiles in a London dry gin, with commonly used botanicals, over the course of a commercial distillation with a focus on the key fractions of distillation: the heads, hearts, and tails.

Materials and methods

Dry gin distillate samples

Distillate samples were collected from an industry standard London dry gin distillation process at Warner's Distillery Ltd. The distillation was performed in a 500 L Arnold Holstein copper pot and column hybrid still over seven hours. The dry gin was prepared using grain neutral spirit diluted to 60% ABV together with the following botanicals: juniper berries, coriander seed, elderflower, black pepper, cardamom pods, cinnamon, angelica root, cassia bark, orange peel, and lemon peel. Samples (200 mL) were collected at the following intervals: when spirit emerged (0 min), the heads cut point (5 min), at 15 minute intervals throughout the heads fraction (15 min - 360 min), at the tails cut point (370 min), and at two more 15 minute intervals in the tails fraction (385 min - 400 min). These sample encompass a standard dry gin distillation. In each distillation replicate, 29 samples were collected. Distillate was sampled in triplicate, from three discrete distillations, with samples sealed in glass storage bottles upon collection. Samples are named: 'distillation fraction_distillation time'. For example, 'Hearts_195' indicates the sample was taken at 195 minutes into the distillation and is part of the hearts fraction.

Preparation of samples

Dry gin distillate samples were diluted from distillation strength (~85% ABV) to 10% ABV with deionised water. A portion (5 mL) of each diluted sample was placed in 20 mL glass headspace vials with an internal standard (2 µg/g 3-heptanone).

Solid-phase micro-extraction gas chromatography-mass spectrometry (SPME-GC-MS)

Volatile compounds in the headspace of the vial were pre-enriched on to a 23-gauge divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) SPME fibre (StableFlex, Sigma Aldrich, Dorset, UK). Each vial was incubated for 5 min at 30°C with an agitation sequence of 10 seconds on, 10 s off. The SPME fibre was then inserted into the vial through the septum and incubated to adsorb volatiles at 30°C for 30 min, while maintaining agitation. Desorption of the volatiles in the inlet was carried out for 1 min at 250°C in the splitless mode.

The volatile compounds within the flavour extracts were separated using a Trace 1300 Gas Chromatograph (Thermo Scientific, Waltham, MA, USA), fitted with a ZB-Wax column (30 m × 0.25 mm ID × 1.0 µm film thickness; Phenomenex, Macclesfield, UK). The injector was operated in splitless mode (240°C, 1 min), with helium carrier gas (18 psi). The oven temperature was programmed as follows: 40°C for 2 min, then a temperature ramp at 6°C/min to 100°C, with an additional temperature ramp at 5°C/min to 230°C, holding for 2 min. All GC effluent was analysed by MS (Thermo Scientific, Waltham, MA, USA). Full scan mode was used to detect the volatile compounds (mass range from m/z 20 to 300).

Identification of compounds

Aroma compounds were tentatively identified from GC-MS analysis by MS library matching and linear retention indices against alkanes (C8-C22) compared to publications on the same WAX phase. Library matches lower than 70% probability were rejected. Each tentatively identified compound was examined further to identify aroma compounds (i.e. to confirm that the compound is perceived to have an aroma) according to the Good Scents Company Information System (http://www.thegoodscentscompany.com). The concentration of the compounds were normalised to a value between zero and one, where one represents the highest concentration of the compound over the hearts fraction, and zero represents the lowest.

Sensory bench testing

Informal descriptive sensory analysis was performed by seven trained distillers as panellists, assessing the aroma of 15 dilute distillate samples (20% ABV), which were representative of the distillation. The samples were:

Heads_0, Heads_Cut, Hearts_15, Hearts_30, Hearts_60, Hearts_90, Hearts_120, Hearts_150, Hearts_180, Hearts_210, Hearts_240, Hearts_270, Hearts_300, Tails_Cut, Tails_15.

The panel were asked to list and describe the aromas they detected in each sample. The aroma descriptors were translated to align with standard aroma descriptors from the Good Scents Company Information System (http://www.thegoodscentscompany.com). For example, 'jasmine' was recorded as a 'floral' aroma. The frequency of detection of each aroma category in each sample was recorded and converted to a percentage value, showing the perception of the aroma category in each sample.

Following GC-MS analysis, the mean concentration of each compound in the hearts distillate (15-360 min) were modelled against the factor of time using Design Expert software (Version 11, StatEase, Minneapolis, USA (Table 1). Where time had a significant effect on the concentration of an identified compound ($p < 0.05$), the model R^2 was maximised. A model $R^2 > 0.8$ was considered sufficient. Statistical details of the models of each compound in distillate samples are reported in Table 2.

Principal Components Analysis (PCA) was performed using XLSTAT software (Addinsoft, SARL, Paris, France) to depict the relationship between the concentration of the 74 identified compounds across the complete range of distillate samples (0-400 min). The sensory bench testing (detailed above) of aroma category frequency of detection across the 15 distillate samples was plotted on the same biplot, presented as secondary data, where the PCA was used as a tool to graphically represent the data.

Agglomerative Hierarchical Clustering (AHC) was performed using XLSTAT software to identify clusters of samples by aroma concentration. This method was also used to identify clusters of aroma categories according to frequency of detection, and samples according to their frequency of aroma category detection.

Results and discussion

Volatile composition of distillate samples

A wide range of aroma compounds (n=74) representing different chemical classes were tentatively identified in the 29 distillate samples (Table 1). In agreement with Dussort et al (2012), terpenes were the most abundent, comprising of monoterpenes (n=19), monoterpenoids (n=12), sesquiterpenes (n=16) and sesquiterpenoids (n=13), . Aldehydes (n=5), ketones (n=3), and esters (n=2) were also identified.

The category and detailed aroma description of the compounds (Table 1) suggests how each compound may contribute to the overall aroma of the distillate. The aroma categories were compiled from Good Scents (http://www.thegoodscentscompany.com), as GC-O was not performed on these samples. Overall, the most frequent aroma category was 'Woody' (n=21), followed by 'Herbal' (n=13) and 'Floral' (n=9) (Table 1).

Dussort et al (2012) previously identified 12 aroma descriptors ('Spicy', 'Floral', 'Microbiological', 'Pungent', 'Chemical', 'Earthy', 'Woody', 'Caramelised', 'Nutty', 'Vegetable', 'Fruity', and 'Unpleasant') in two commercial gins by GC-O which aligns with compounds identified in Table 1. The compounds had a broad range of different physicochemical properties (Table 1). A compound's log P value indicates its solubility in water by giving the logarithm of the octanal-water partition coefficient, such that a compound with low water solubility has a high log P. The vapour pressure of a compound denotes its volatility, by indicating the tendency of the compound to change into a gaseous or vapour state, where higher vapour pressure implies higher volatility. In general, with increasing compound retention time, log P increases and vapour pressure decreases (Table 1).

Table 1a.

Monoterpenes tentatively identified in distillate samples

a. Monoterpenes [*] Compound	CAS	Aroma Category [a]	Aroma Description [b]	Identification Ion	R_t [c]	Log P [d]	Vapour Pressure (mm Hg at 25 ˚C) [e]
alpha-Pinene	80-56-8	Herbal	Herbal	93	7.48	4.44	4.75
alpha-thujene	2867-05-2	Woody	Woody, Green, Herbal	91	7.71	4.61	4.77
alpha-fenchene	471-84-1	Camphoreous	Camphoreous	79	8.71	4.35	3.38
Camphene	79-92-5	Woody	Woody	93	8.97	4.35	3.00
(-)-beta-Pinene	18172-67-3	Herbal	Herbal	93	10.39	4.35	2.40
Sabinene	3387-41-5	Woody	Woody	51	11.14	4.69	2.63
3-Carene	13466-78-9	Citrus	Citrus, Herbal, Pine, Resinous, Woody	93	12.07	4.61	3.72
Myrcene	123-35-3	Spicy	Spicy	93	12.64	4.33	2.29
alpha-Terpinene	99-86-5	Woody	Woody	121	13.27	4.75	1.64
(R)-(+)-Limonene	5989-27-5	Citrus	Citrus, Orange, Fresh, Sweet	68	13.95	4.83	0.20
beta-Phellandrene	555-10-2	Minty	Minty	93	14.43	4.70	1.57
trans-beta-Ocimene	3779-61-1	Sweet	Sweet, Herbal	93	15.29	4.88	1.56
gamma-Terpinene	99-85-4	Terpenic	Terpenic	93	15.82	4.75	1.08
beta-Ocimene	13877-91-3	Floral	Floral, Citrus, Tropical, Green, Woody	93	15.87	4.80	1.56
para-Cymene	99-87-6	Terpenic	Terpenic	119	16.71	4.10	1.46
Terpinolene	586-62-9	Herbal	Herbal	93	17.12	4.47	1.13
(E)-sabinene hydrate	17699-16-0	Woody	Woody, Balsam	43	17.40	3.19	0.08
1,5,8-para-menthatriene	21195-59-5	Roasted	Roasted	134	21.22	4.62	1.28
Geranyl acetate	105-87-3	Floral	Floral, Rose, Lavender, Green, Waxy	69	32.94	3.98	0.03

Table 1b.

Monoterpenoids tentatively identified in distillate samples

b. Monoterpenoids [*] Compound	CAS	Aroma Category [a]	Aroma Description [b]	Identification Ion	R_t [c]	Log P [d]	Vapour Pressure (mm Hg at 25 ˚C) [e]
Eucalyptol	470-82-6	Herbal	Herbal	84	14.12	2.74	1.90
Sabinene hydrate	546-79-2	Herbal	Herbal, Minty	71	15.20	3.19	0.08
Linalyl butyrate	78-36-4	Floral	Floral, Bergamot, Tropical Fruit, Citrus	71	18.21	5.37	0.01
Perillene	539-52-6	Woody	Woody	69	22.05	4.21	0.95
alpha-Terpineol	98-55-5	Terpenic	Terpenic, Pine, Citrus, Woody, Floral	59	22.92	3.28	0.03
dextro-Camphor	464-49-3	Camphoreous	Camphoreous	95	25.64	3.04	4.00
Linalool	78-70-6	Floral	Floral, Citrus, Sweet, Rose, Woody, Green	71	26.24	2.97	0.02
Methyl citronellate	2270-60-2	Floral	Floral	69	26.85	4.07	0.08
Citronellyl acetate	150-84-5	Floral	Floral, Green, Rose, Fruity, Citrus, Woody	82	29.98	4.56	0.05
Neral	106-26-3	Citrus	Citrus, Sweet, Lemon Peel	69	30.87	3.45	0.07
alpha-Terpinyl acetate	80-26-2	Herbal	Herbal, Bergamot, Lavender, Citrus	121	31.37	3.96	0.04
L-Borneol	464-45-9	Balsamic	Balsamic	95	31.47	2.69	0.04

Table 1c.

Sesquiterpenes tentatively identified in distillate samples

c. Sesquiterpenes [*] Compound	CAS	Aroma Category [a]	Aroma Description [b]	Identification Ion	R_t [c]	Log P [d]	Vapour Pressure (mm Hg at 25 ˚C) [e]
alpha-Cubebene	17699-14-8	Herbal	Herbal, Waxy	161	23.23	6.73	0.01
delta-Elemene	20307-84-0	Herbal	Herbal, Sweet, Woody	121	23.66	6.96	0.03
alpha-Copaene	3856-25-5	Woody	Woody, Spicy, Honey	161	24.51	5.71	0.04
beta-cubebene	13744-15-5	Citrus	Citrus, Fruity, Radish	161	26.08	6.13	0.01
(E)-alpha-bergamotene	13474-59-4	Woody	Woody, Warm, Tea	95	27.60	6.54	0.02
(-)-beta-elemene	515-13-9	Sweet	Sweet	81	27.88	7.04	0.03
beta-caryophyllene	87-44-5	Spicy	Spicy, Sweet, Woody, Clove, Dry	133	28.28	6.30	0.01
(-)-gamma-elemene	29873-99-2	Green	Green, Oily, Woody	121	29.39	6.49	-
(E)-beta-Famesene	18794-84-8	Woody	Woody, Citrus, Herbal, Sweet	69	30.06	7.14	0.01
alpha-Humulene	6753-98-6	Woody	Woody	93	30.58	6.95	0.01
gamma-muurolene	30021-74-0	Woody	Woody, Herbal, Spicy	161	31.07	6.55	0.01
(E)-Germacrene D	23986-74-5	Woody	Woody	161	31.81	6.99	0.01
alpha-Muurolene	10208-80-7	Woody	Woody	105	32.15	6.19	0.01
alpha-Gurjunene	489-40-7	Woody	Woody, Balsam	81	32.16	6.18	0.02
bicyclogermacrene	24703-35-3	Green	Green, Woody, Weedy	121	32.56	6.22	0.01
alpha-curcumene	644-30-4	Herbal	Herbal	132	33.59	6.27	0.01

Table 1d.

Sesquiterpenoids tentatively identified in distillate samples

d. Sesquiterpenoids [ǂ] Compound	CAS	Aroma Category [a]	Aroma Description [b]	Identification Ion	R_t [c]	Log P [d]	Vapour Pressure (mm Hg at 25 ˚C) [e]
Isocaryophyllene	118-65-0	Woody	Woody, Spicy	175	27.41	6.30	0.01
alpha-Santalene	512-61-8	Woody	Woody	120	32.11	6.43	0.04
(R)-gamma-cadinene	39029-41-9	Woody	Woody, Herbal	161	33.31	6.27	0.01
alpha-cadinene	24406-05-1	Woody	Woody, Dry	105	34.27	6.56	0.01
germacrene B	15423-57-1	Woody	Woody, Earthy, Spicy	121	35.50	7.18	0.00
Calamenene	483-77-2	Herbal	Herbal, Spice	159	35.51	6.25	0.01
alpha-Calacorene	21391-99-1	Woody	Woody	157	37.98	6.22	0.00
beta-Caryophyllene oxide	1139-30-6	Woody	Woody, Sweet, Fresh, Dry, Spicy	79	39.93	4.91	0.01
(E)-nerolidol	40716-66-3	Floral	Floral, Green, Citrus, Woody, Waxy	69	40.81	5.68	0.00
Spathulenol	6750-60-3	Earthy	Earthy	205	43.41	4.63	0.00
tau-cadinol	5937-11-1	Balsamic	Balsamic, Earthy	161	44.55	4.90	-
tau-muurolol	19912-62-0	Herbal	Herbal, Spicy, Honey	95	44.95	4.95	0.00
alpha-cadinol	481-34-5	Herbal	Herbal, Woody	95	46.09	4.90	-

Table 1e.

Aldehydes, ketones, esters and other compounds tentaively identified in distallate samples

e. Aldehydes, Ketones, Esters, and others Compound	CAS	Aroma Category [a]	Aroma Description [b]	Identification Ion	R_t [c]	Log P [d]	Vapour Pressure (mm Hg at 25 ˚C) [e]
Aldehydes [ǂ]							
Octanal	124-13-0	Aldehydic	Aldehydic	56	17.30	2.78	2.07
nonanal	124-19-6	Aldehydic	Aldehydic	56	21.08	3.27	0.53
(+)-alpha-campholenic aldehyde	4501-58-0	Herbal	Herbal	108	24.65	3.31	0.42
decanal	112-31-2	Aldehydic	Aldehydic	43	24.74	3.76	0.21
(Z)-cinnamaldehyde	57194-69-1	Spicy	Spicy, Cinnamon	131	41.55	2.12	0.03
Ketones [ǂ]							
Acetone	67-64-1	Solvent	Solvent	43	2.99	-0.24	232.00
undecan-2-one	112-12-9	Fruity	Fruity, Waxy, Creamy, Orris, Floral	58	28.01	4.09	0.10
1-(4-hydroxyphenyl)ethanone	99-93-4	Floral	Floral, Sweet, Balsamic	121	33.08	1.35	0.00
Esters [ǂ]							
octyl acetate	112-14-1	Floral	Floral, Green, Earthy, Mushroom	61	23.81	3.81	0.19
Methyl (E)-cinnamate	1754-62-7	Balsamic	Balsamic, Sweet, Strawberry, Cherry	131	42.39	2.62	0.01
Others [ǂ]							
Toluene	108-88-3	Sweet	Sweet	91	8.39	2.73	27.71
2,3-dihydro-1,8-cineole	92760-25-3	Minty	Minty, Lemon	109	13.50	2.51	1.24
tert-butanol	75-65-0	Camphoreous	Camphoreous	59	15.67	0.73	40.70
Styrene	100-42-5	Balsamic	Balsamic, Sweet	104	16.26	2.89	6.21

[ǂ] Compound category colours correspond to those in Figure 4.

[a, b] Aroma categories and descriptors from Good Scents (http://www.thegoodscentscompany.com).

[c] Retention time of compound on a ZB-WAX Column.

[d, e] Log P and vapour pressure from Good Scents (http://www.thegoodscentscompany.com).

Clustering of fractions throughout distillation

Agglomerative Hierarchical Clustering (AHC) analysis was performed (Figure 1) which merges the most similar clusters together, starting with each data point as a separate cluster. The full set of 29 distillate samples are separated into four clusters (Figure 1) with clustering driven by the distillation time. However, there were some differences. For example the hearts fraction was separated into two distinct clusters; and the volatile composition of the tails samples was more similar to the earlier hearts samples than the late hearts samples.

The changes in concentration of the 74 aroma compounds over 15 distillates are illustrated using PCA (Figure 2), together with the result of the sensory bench testing. Principal Component 1 and Principal Component 2, account respectively for 50.9% and 23.1% of the variation. Principal Component 1 mainly separates the head samples to the tails samples (Tails_Cut and Tails_15 contribute 37.1% and 23.8%). Principal Component 2 separates heads and tail samples (Heads_0 and Tails_15 contribute 22.2% and 28.3%).

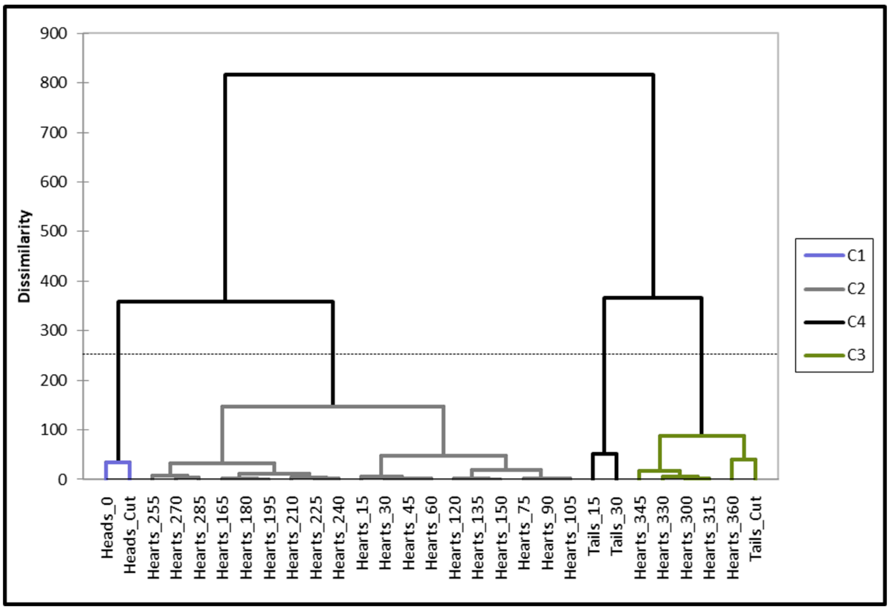
The hearts fraction samples do not represent the extremes of flavour volatile composition. These samples load the most centrally of all the samples in the set (Figure 2). Whereas the heads and tails samples do represent these extremes of flavour volatile composition, characterised by the samples loading at the extremities of the bipot. This supports the view that the hearts fraction are desirable due to the flavour characteristics not being influenced by higher concentrations of undesirable volatiles present in the later hearts and tails distillate (Lukić et al. 2011). However, the variation within the hearts fraction illustrates the potential for additional control over aroma profile by selection and re-blending of different distillation fractions.

Kinetics of aroma compounds throughout distillation

The hearts fraction forms the final spirit and determines its organoleptic qualities. Accordingly, the hearts fractions (Hearts_15 to 360) and compounds that were defined as being out of the modellable range (i.e. an insufficient R^2 value) were excluded (see Supplementary Information). The release kinetics of key volatiles for the hearts range were modelled and the resulting 53 models are

Figure 1.

Dendrogram from AHC analysis, clustering 29 distillate samples according to the mean concentration of 74 aroma compounds.



presented in Table 2. All the compound categories are represented (monoterpenes (n=16), sesquiterpenes (n=14), monoterpenoids (n=7), sesquiterpenoids (n=7), aldehydes (n=4), ketones (n=1), esters (n=1), and others (n=2)) (Table 2).

The models had a high significance (p <0.0001), with the majority cubic models (n=38 of 53 compounds), or quadratic models (n=14), with only one fitting to a linear model (Table 2). All compounds (n=53) were clustered using Agglomerative Hierarchical Clustering (Figure 3) and formed three distinct clusters: Cluster 1 contained 14 compounds, Cluster 2 contained five compounds and Cluster 3 contained 34 compounds. Compounds in Cluster 1 decreased in concentration over the hearts fraction (Figure 4a), compounds in Cluster 2 increased throughout the hearts fraction (Figure 4b) and compounds in Cluster 3 increased in the later stages of the hearts fraction (Figure 4c). Greer et al (2008) noted that monoterpenes can be precursors to off-flavours in finished gins. This is because, like most terpenes, they are thermally unstable, decomposing or oxidising at high temperatures or in the presence of light or oxygen (Hanci et al. 2003; Almeida et al. 2018). This changes their aroma characteristics, which in some cases are undesirable. Hancı et al (2003) suggested increasing the rate of distillation to reduce the volume of monoterpenes in the distillate. In addition, Greer et al (2008) noted that gin produced by vacuum distillation compared to traditional distillation contained less monoterpenes, which resulted in more desirable aroma characteristics with less nasal pungency. Delaying the heads cut point would reduce the volume of monoterpenes in the hearts (Figure 4a).

It is noted that early fractions of gin distillates are principally composed of juniper components (Clutton and Evans 1978). As the flavour of juniper must be prominent in gin by law, delaying the cut point of the heads may reduce the perception of juniper characteristics (EU 2008). For example, a-pinene is known to contribute significantly to the flavour of juniper (Clutton and Evans 1978: Greer et al. 2008: Hodel et al. 2020), and is identified as a compound that decreases in concentration in the distillate over the hearts fraction (Figure 4a). Delaying the heads cut point would reduce the concentration of a-pinene in the final spirit but would remain perceptible as the detection threshold of a-pinene is 1650 µg/L (Riu-Aumatell et al. 2008). This would be met if only the two

Figure 2.

PCA biplot (PC1 and PC2) of the mean concentration of 74 aroma compounds and frequency of detection of aroma category by sensory bench testing in 15 distillate samples.

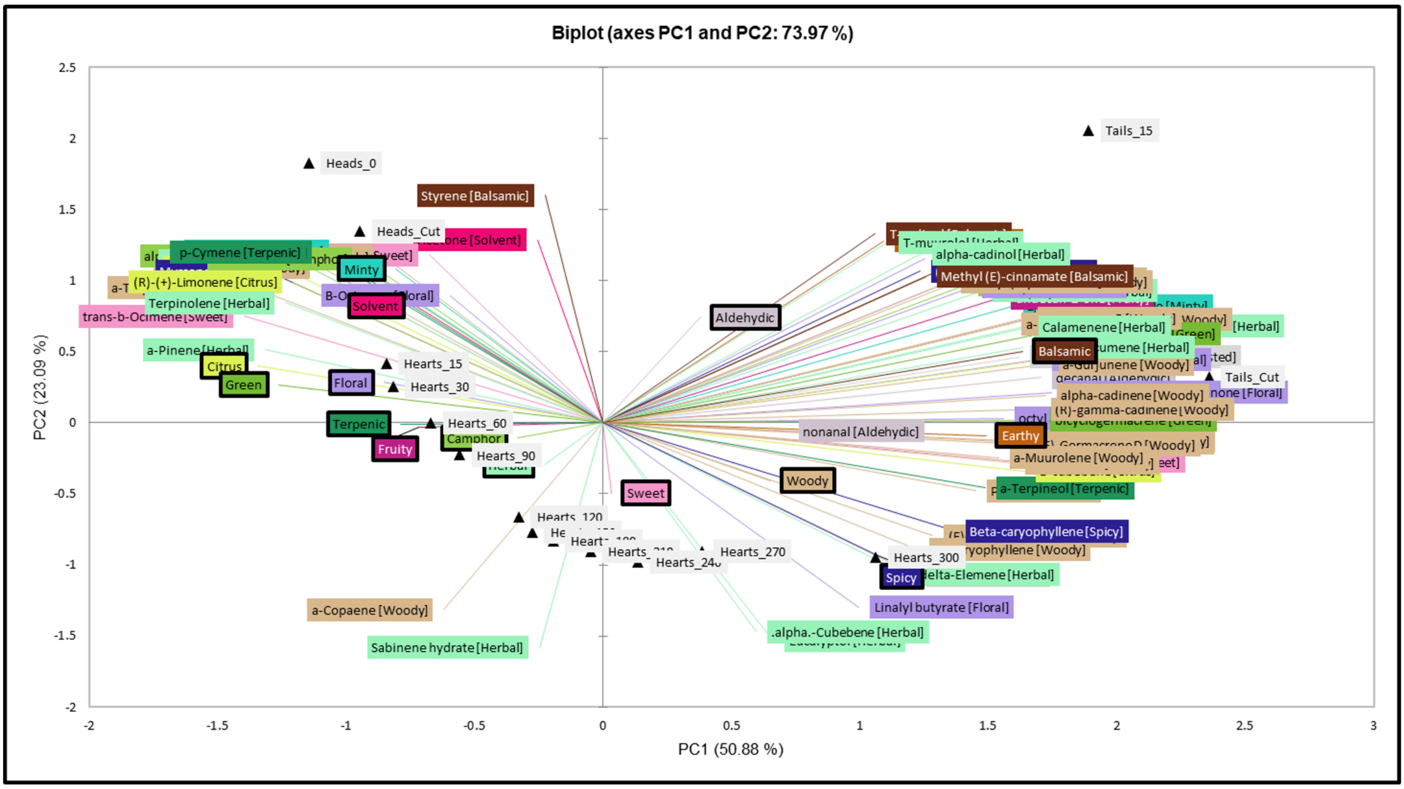


Table 2. **Model fit data for compound concentration over distillation time**

Values in **bold** are statistically significant ($p < 0.05$)

2a - Monoterpenes

Model Component	alpha-Pinene [Herbal]	alpha-thujene [Woody]	alpha-fenchene [Camphoreous]	Camphene [Woody]	(-)-beta-Pinene [Herbal]	3-Carene [Citrus]	Myrcene [Spicy]	alpha-Terpinene [Woody]	(R)-(+)-Limonene [Citrus]	beta-Phellandrene [Minty]	gamma-Terpinene [Terpenic]	beta-Ocimene [Floral]	para-Cymene [Terpenic]	(E)-sabinene hydrate [Woody]	1,5,8-para-menthatriene [Roasted]	Geranyl acetate [Floral]
Model	Quadratic	Quadratic	Cubic	Cubic	Cubic	Cubic	Quadratic	Quadratic	Cubic	Cubic	Cubic	Quadratic	Cubic	Quadratic	Cubic	Cubic
Model p Value	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Model R^2	0.9443	0.9422	0.9701	0.9403	0.9735	0.9319	0.9414	0.8137	0.948	0.941	0.9615	0.8796	0.9861	0.9571	0.8108	0.9534
A p Value	**<0.0001**	**<0.0001**	**<0.0001**	0.5331	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0185**	**0.047**	**0.0023**	**<0.0001**	**<0.0001**	**<0.0001**	0.239	0.1085
A^2 p Value	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0017**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0457**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
A^3 p Value	-	-	**0.0214**	**<0.0001**	**0.009**	**0.0231**	-	-	**0.0013**	**<0.0001**	**0.0003**	-	**<0.0001**	-	**0.0009**	**<0.0001**

2b - Sesquiterpenes

Model Component	delta-Elemene [Herbal]	beta-cubebene [Citrus]	(E)-alpha-bergamotene [Woody]	(-)-beta-elemene [Sweet]	beta-caryophyllene [Spicy]	(-)-gamma-elemene [Green]	(E)-.beta.-Famesene [Woody]	alpha-Humulene [Woody]	gamma-muurolene [Woody]	(E)-Germacrene D [Woody]	alpha-Muurolene [Woody]	alpha-Gurjunene [Woody]	bicyclogermacrene [Green]	alpha-curcumene [Herbal]
Model	Linear	Quadratic	Cubic	Cubic	Quadratic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic
Model p Value	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Model R^2	0.86543	0.9582	0.9751	0.9875	0.9648	0.9912	0.984	0.9887	0.971	0.99	0.9794	0.9818	0.9898	0.9777
A p Value	**<0.0001**	**<0.0001**	**0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	0.0746
A^2 p Value	-	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
A^3 p Value	-	-	**<0.0001**	**0.0068**	-	**<0.0001**	**0.0099**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0495**	**0.0426**	**<0.0001**	**<0.0001**

2c - Monoterpenoids and sesquiterpenoids

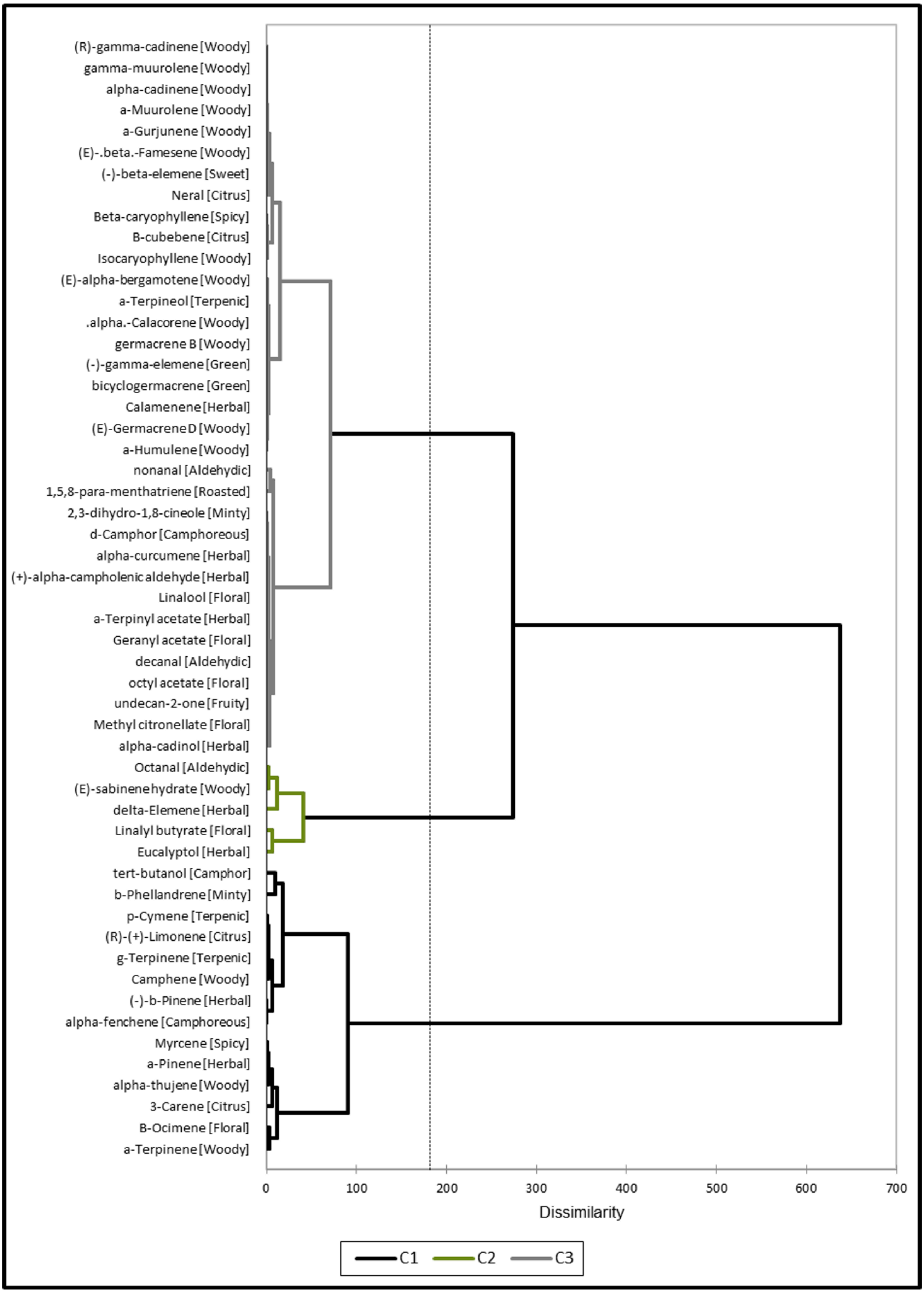
Model Component	Eucalyptol [Herbal]	Linalyl butyrate [Floral]	alpha-Terpineol [Terpenic]	dextro-Camphor [Camphoreous]	Linalool [Floral]	Methyl citronellate [Floral]	Neral [Citrus]	alpha-Terpinyl acetate [Herbal]	Isocaryophyllene [Woody]	(R)-gamma-cadinene [Woody]	alpha-cadinene [Woody]	germacrene B [Woody]	Calamenene [Herbal]	alpha-Calacorene [Woody]	alpha-cadinol [Herbal]
Model	Cubic	Quadratic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Quadratic	Quadratic	Cubic	Cubic	Cubic	Cubic	Quadratic
Model p Value	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Model R^2	0.919	0.904	0.9735	0.9814	0.9717	0.9182	0.9561	0.9512	0.917	0.9706	0.9828	0.9878	0.9774	0.9818	0.8814
A p Value	**<0.0001**	**<0.0001**	**<0.0001**	**0.0130**	0.4091	0.6682	**<0.0001**	0.0674	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0003**	**<0.0001**
A^2 p Value	**0.0001**	0.1316	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
A^3 p Value	0.0819	-	**0.0020**	**<0.0001**	**<0.0001**	**<0.0001**	0.7302	**<0.0001**	-	-	**0.0059**	**<0.0001**	**0.0014**	**<0.0001**	-

2d - Aldehydes, ketones, esters, and others

Model Component	Eucalyptol [Herbal]	Linalyl butyrate [Floral]	alpha-Terpineol [Terpenic]	dextro-Camphor [Camphoreous]	Linalool [Floral]	Methyl citronellate [Floral]	Neral [Citrus]	alpha-Terpinyl acetate [Herbal]	Isocaryophyllene [Woody]	(R)-gamma-cadinene [Woody]	alpha-cadinene [Woody]	germacrene B [Woody]	Calamenene [Herbal]	alpha-Calacorene [Woody]	alpha-cadinol [Herbal]
Model	Cubic	Quadratic	Cubic	Cubic	Cubic	Cubic	Cubic	Cubic	Quadratic	Quadratic	Cubic	Cubic	Cubic	Cubic	Quadratic
Model p Value	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
Model R^2	0.919	0.904	0.9735	0.9814	0.9717	0.9182	0.9561	0.9512	0.917	0.9706	0.9828	0.9878	0.9774	0.9818	0.8814
A p Value	**<0.0001**	**<0.0001**	**<0.0001**	**0.0130**	0.4091	0.6682	**<0.0001**	0.0674	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**0.0003**	**<0.0001**
A^2 p Value	**0.0001**	0.1316	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**	**<0.0001**
A^3 p Value	0.0819	-	**0.0020**	**<0.0001**	**<0.0001**	**<0.0001**	0.7302	**<0.0001**	-	-	**0.0059**	**<0.0001**	**0.0014**	**<0.0001**	-

Figure 3.

Dendrogram from AHC analysis, clustering of 53 aroma compounds according to their mean concentration in 24 heart distillate samples (15-360 min).



hearts samples containing the lowest concentration of a-pinene in this study were mixed to create a final spirit. In the GC-Olfactometry analysis of two Bavarian gin samples, a-pinene was identified as odour active, yielding high flavour dilution factors which imply the influence on the overall aroma of gin (Buck et al. 2020). This, however, is most likely due to the high concentration of a-pinene collected from the still at the earlier stages of distillation which remain in the final spirit.

The monoterpenes in juniper can vary with origin, but typically include p-cymene, myrcene, g-terpinene, a-pinene, and limonene (forming 70% of the volatile composition of juniper) (Vichi et al. 2007; Greer et al. 2008). However, the volatile composition of juniper includes up to 190 volatile compounds, which were identified in juniper berry oil by Robbat et al (2011) using two-dimensional gas chromatography. While many of the monoterpenes in Figure 4a are key odorants in juniper, they are also found in other botanicals. Key aroma volatiles in angelica root (used in this study) include a-pinene, sabinene (identified in Table 1 and Figure 2), and 3-carene (Holm et al. 1997). As with any ingredient of botanical origin, volatile composition varies between types. Gamma-terpinene, a key odorant in juniper and coriander seed, has an odour threshold of 1.5 µg/g (Clutton and Evans 1978). When considering distillation (Figure 2), this concentration is found in the earliest stages of the hearts fraction but increased in the heads fraction. The model for the concentration of g-terpinene over the hearts fraction is cubic ($p < 0.0001$), it decreases rapidly in the first 150 minutes of the hearts fraction and remains at a low level over the remaining 195 minutes of the fraction. This general model is shared by most of the compounds in Cluster 1, where concentration decreases rapidly in the earlier stages of the hearts fraction. Compounds in Cluster 2 (n=5) increased in concentration gradually over the hearts fraction (Figure 4b) and includes two monoterpenoids (eucalyptol and linalyl butyrate), one monoterpene ((E)-sabinene hydrate), one sesquiterpene (delta-elemene) and one aldehyde (octanal). There are three sub-clusters: (1) eucalyptol and linalyl butyrate (monoterpenoids) increase in concentration rapidly over the hearts fraction; (2) octanal and (E)-sabinene (hydrate form) fit quadratic models (both $p < 0.0001$) but follow a slower initial increase in concentration with their final concentration being the highest; (3) delta-elemene increases consistently over extraction and follows the only linear model in the entire set ($p < 0.0001$).

Eucalyptol is the only volatile in the cluster to follow a cubic model ($p < 0.0001$). The concentration of eucalyptol increased gradually over the hearts fraction - peaking at Hearts_255 - then decreasing slowly with increasing distillation time. Almeida et al (2018) noted that eucalyptol concentration increased over time in a steam distillation. The current model for eucalyptol concentration during commercial distillation substantiates this, adding detail to the extraction kinetics due to the high sampling frequency.

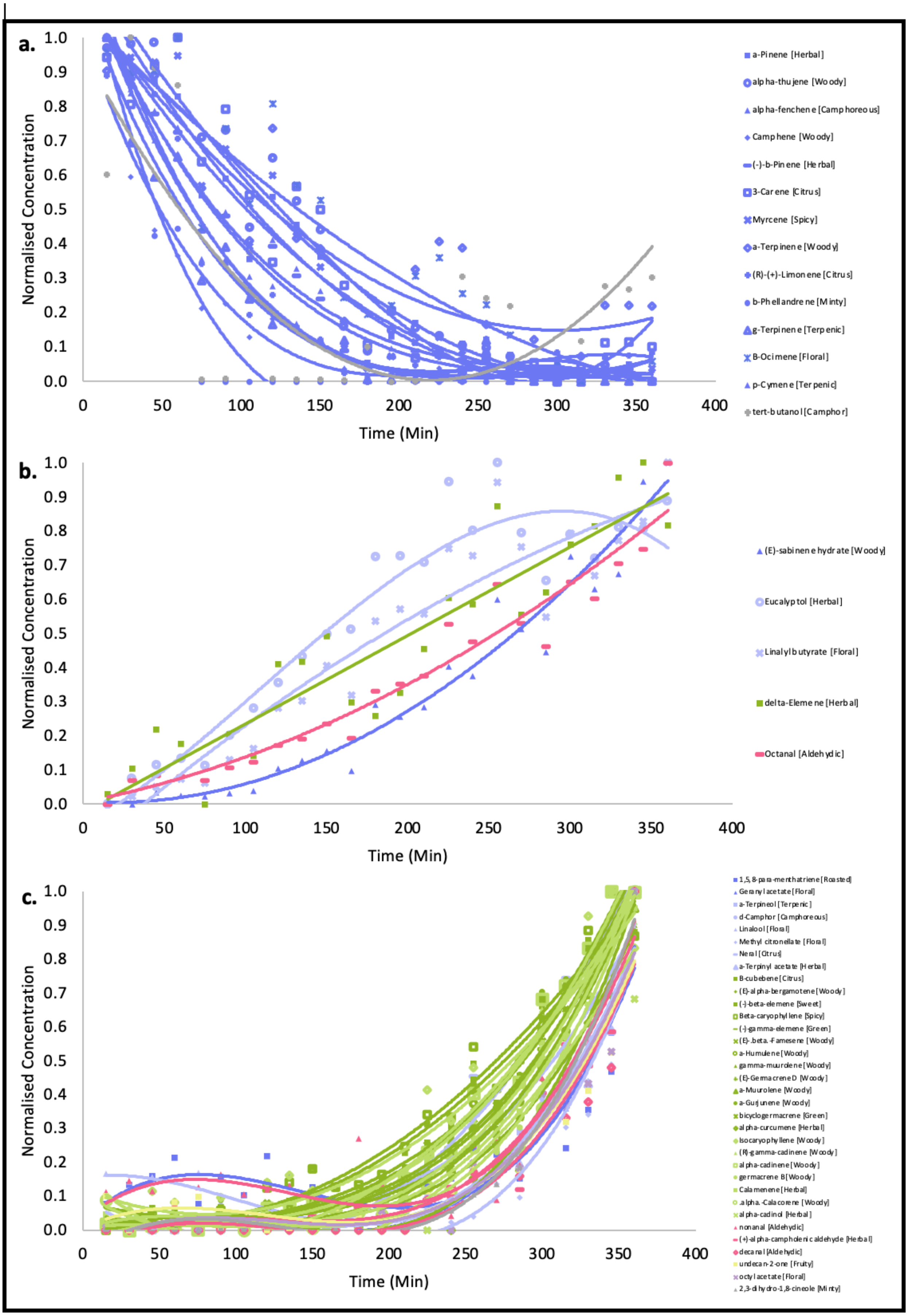
Compounds in Cluster 3 (n=34) increased in concentration in the latter half of the hearts fraction (Figure 4c). Compounds predominantly include sesquiterpenes (n=13), sesquiterpenoids (n=7), and monoterpenoids (n=6); monoterpenes (n=2), aldehydes (n=3), ketones (n=1), and esters (n=1) in Cluster 3.

As an exemplar sesquiterpene, the extraction of beta-caryophyllene increased rapidly after 200 minutes of distillation, fitting a quadratic model ($p < 0.0001$). This general model is shared by the remaining compounds found in Cluster 3 (Figure 4c). Previous investigations into the flavour of gin have shown similar results for sesquiterpenes. Gamma-muurolene was identified by Clutton and Evans (1978) to be the principal sesquiterpene in ethanolic juniper distillates, reaching the highest concentration in the later stage of distillation. Hodel et al (2021) modelled the behaviour of selected volatile terpenes in a model gin system and reported that beta-caryophyllene increased in concentration over the four collected fractions.

In steam distillation of essential oil from thyme, sesquiterpenes were shown to elute in later distillation fractions (Hancı et al. 2003). The study reported here, builds on these studies through a greater sampling frequency, which results in a significant improvement in the kinetic models.

Figure 4.

Normalised compound concentration over distillation time in 24 heart distillate samples (15-360 min) (Figure 4a: Cluster 1; Figure 4b: Cluster 2; Figure 4c: Cluster 3).



As an exemplar monoterpene, linalool is the principal volatile from coriander seed and increases in concentration during gin distillation (Clutton and Evans 1978; Greer et al. 2008). This was also found in this study where linalool fits a complex cubic model ($p < 0.0001$), where the concentration initially decreased in the first hearts distillate samples (15 – 165 minutes), then increased rapidly to the final Hearts_360 sample (Figure 4c). Alpha-terpinol, an oxygenated monoterpene (classified as a monoterpenoid), is a known constituent of juniper essential oil (Markovic et al. 2017). Alpha-terpinol increased in concentration in the later stages of the hearts fraction (Figure 4c). In aqueous steam distillation of thyme for essential oil, oxygenated monoterpenes were most rapidly recovered from the still despite their high boiling points (Hancı et al. 2003). However, in this study, the modelled monoterpenoids (excluding monoterpenes) had the highest concentrations in the latest stages of the hearts fraction (Figure 4). This is likely to be due to the different solvent used. In this study, both ethanol and water were used, whereas Hancı et al (2003) used only water during steam distillation. This highlights the commercial relevance of this study to the gin industry and the importance of not transferring kinetic extraction models from studies where different solvent systems are used.

Cluster 3 has the highest LogP (LogP 5.26, n=34), whereas Cluster 1 (LogP 4.26, n=14) and Cluster 2 (LogP 4.21, n=5) have similar mean LogP values for the modelled compounds. Although compounds in Cluster 1 were the most water soluble, they are also the most volatile, causing them to elute from the still with the highest concentration in the earlier stages of distillation (Figure 4a). In contrast, compounds in Cluster 3 (Figure 4c) have a low volatility and are less soluble in water. The low volatility of these compounds has a greater influence on their elution from the still than their water solubility and they less readily leave the water/ethanol/volatile mixture. Consequently, these compounds appear in higher concentrations in the later stages of distillation. Compounds modelled in Cluster 2 (Figure 4b) increased in elution from the still during the hearts fraction, perhaps reflecting their intermediate physicochemical properties. Compounds in this cluster have similar water solubility (lower log P) to compounds in Cluster 1, yet also share similarities in volatility (low vapour pressure) with compounds in Cluster 3.

The release of the modelled compounds of Cluster 2 may be further influenced by the gradual increase in still temperature over distillation together with changes in the concentration of ethanol and water over distillation. Increasing the still temperature encourages compounds to volatilise, while an increasing water concentration (due to decreasing ethanol concentration) allows more water-soluble compounds to remain in the solvent mixture until sufficient temperature is achieved, which encourages these compounds (with lower LogP) to volatilise later in distillation.

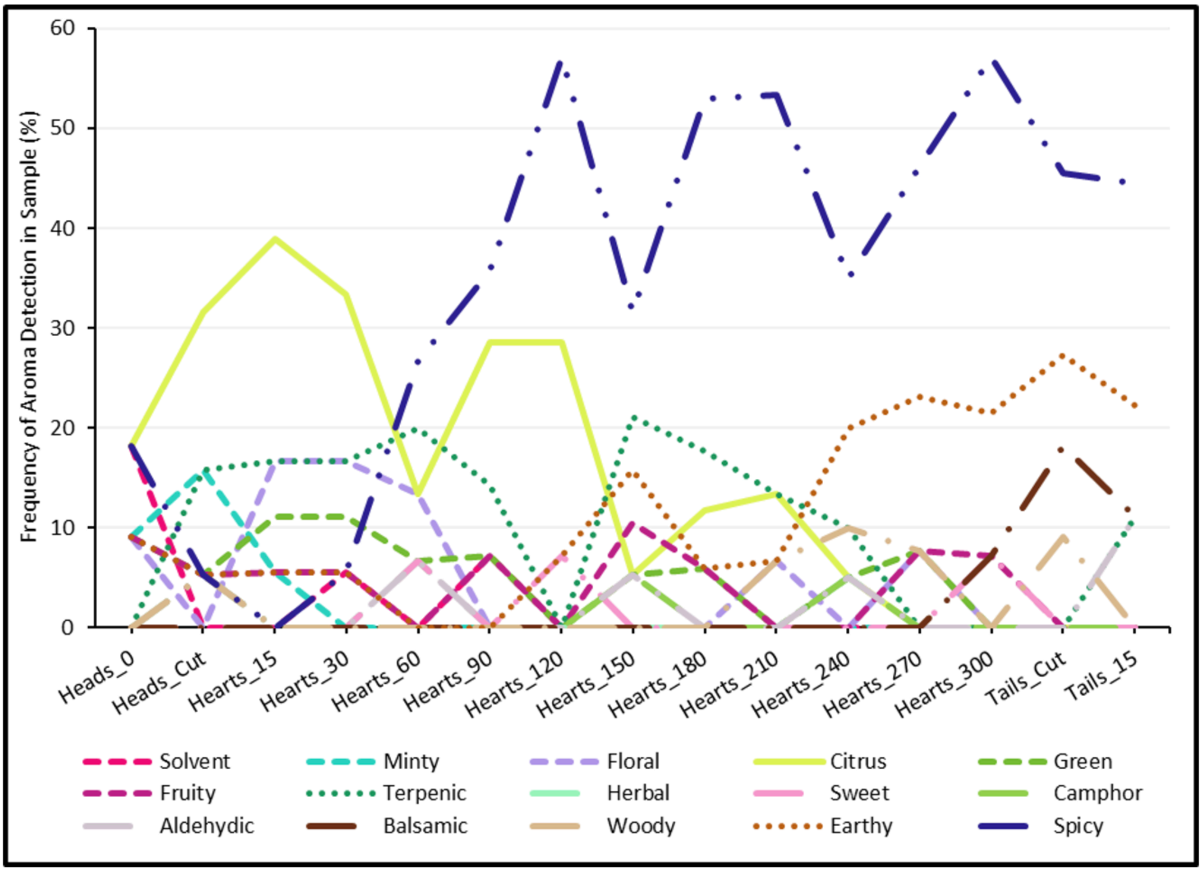
Association of aroma characteristics with volatile composition over distillation by informal sensory bench testing

Informal sensory bench testing was used to evaluate the frequency of detection of 15 aroma characteristics across the distillation fractions (Figure 5). Attributes were used and samples clustered using Agglomerative Hierarchical Clustering (AHC) (Figure 6a). Attributes were clustered into two main groups (1) Spicy and (2) all other attributes.

Distillate samples were analysed by AHC according to their frequency of aroma category detection (Figure 6b). The analysis yielded three clusters. Cluster 1 was characterised by higher frequency of detection of ‘Floral’, ‘Green’, ‘Solvent’, and ‘Citrus’ characteristics. Cluster 2 is had a higher frequency of detection of ‘Camphor’, ‘Herbal’, ‘Aldehydic’ and ‘Terpenic’ aroma categories (Figure 6b). Cluster 3 exhibited a higher frequency of detection of the ‘Spicy’, ‘Balsamic’, ‘Earthy’ and ‘Sweet’ aroma characteristics. The impact of distillation on the abundance of volatile aroma compounds and the frequency of detection of sensory descriptors is summarised using PCA (Figure 2). The first two Principal Components explained 74.0% of the data (50.9% and 23.1% respectively) (Figure 2). ‘Balsamic’, ‘Earthy’ and ‘Spicy’ are strongly positively resolved on PC1 whereas ‘Citrus’ and ‘Green’ are strongly negatively resolved on PC1. ‘Floral’, ‘Minty’, ‘Solvent’, ‘Terpenic’ and ‘Fruity’ are also negatively resolved on PC1 but less strongly. ‘Spicy’ is further resolved negatively on PC2.

Figure 5.

Frequency (%) of aroma category detection in each distillate sample (n=15).



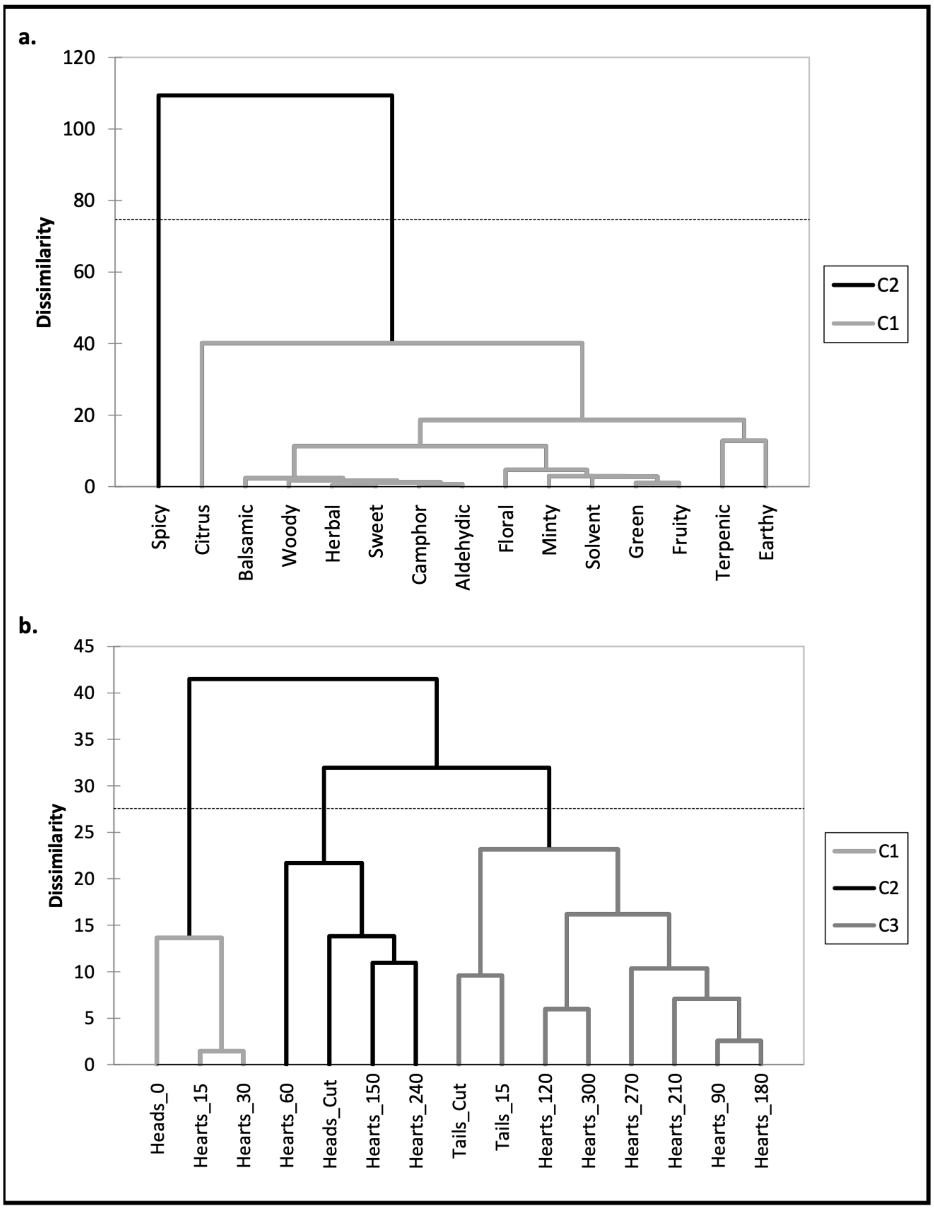
The perception of ‘Citrus’ in the earlier distillate samples may reflect the high concentrations of (R)-(+)-limonene and 3-carene. Notably, limonene ((R)-(+)-limonene) was reported as one of the key terpenes modelled in a gin distillation by Hodel et al (2021), and was also listed as a representative compound in the characterisation of dry gin volatiles (Vichi et al. 2005). This volatile can be highly odour active (FD factor ≥2048), depending on the gin (Buck et al. 2020). It was also noted by Clutton and Evans (1978) that gins with ‘orange’ characteristics contain a high concentration of limonene, which is present above its threshold of perception.

The compound responsible for the ‘Solvent’ aroma is likely to be acetone, which is associated with higher concentrations in the heads samples. ‘Spicy’ is correlated with beta-caryophyllene, which has ‘Spicy, Sweet, Woody, Clove, and Dry’ attributes (Table 1). Furthermore, it has been described as having a ‘woody’ and ‘spice’ aroma (Vichi et al. 2007) and has been shown to be a key gin terpene by Hodel et al (2021). Therefore, it is likely that beta-caryophyllene is responsible for the ‘spicy’ attribute. However, it may also contribute to the ‘Woody’ and ‘Sweet’ attributes as well. Beta-caryophyllene is in Cluster 3 of the aroma kinetic groups suggesting it is released later in the extraction process which aligns with the frequency of detection of ‘spicy’ and ‘woody’.

The majority (60%) of the freshest aroma descriptors: ‘Minty’, ‘Solvent’, ‘Citrus’, ‘Green’, ‘Floral’, ‘Terpenic', ‘Fruity’, ‘Camphor’ and ‘Herbal’ load negatively on PC1 (Figure 2). The earliest distillate samples, (Heads_0 to Hearts_210) also load negatively on PC1. Therefore, these early distillate samples are more likely to express fresher characteristics than the later samples, which are likely a result of the differential concentration of volatile aromas (e.g. greater abundance of monoterpenes). As distillation time increases, the aroma descriptors ‘Sweet’, ‘Woody’, ‘Spicy’, ‘Earthy’, Aldehydic’, and ‘Balsamic’ are more likely to be used to describe the samples (Hearts_240 to Tails_15), these are positively projected on PC1 and are likely to reflect the greater abundance of sesquiterpenes and sesquiterpenoids.

Figure 6.

Dendrograms from AHC analysis, clustering aroma categories according to frequency of detection across 15 samples (Figure 6a), clustering distillate samples according to their frequency of aroma category detection (Figure 6b)



Conclusions

For the first time, distillate flavour over regular intervals was investigated during the commercial distillation of dry gin. Although distillers use three major fractions of distillation to determine the collection of desirable spirit (and the resultant organoleptic quality), this work identified four fractions from the composition of aroma volatiles. Understanding the progression of the volatile composition during distillation has the potential to tailor the organoleptic characteristics of the spirit by modifying the distillation cut points to collect more desirable volatiles.

Seventy-four volatile compounds were tentatively identified by HS-SPME-GC-MS across 29 distillate samples. Four clusters were identified: heads, early hearts, late hearts, and tails. The samples from the hearts fraction were examined further, modelling 53 aroma volatiles which would elute from the still at the greatest concentration either in the earlier or later stages of the fraction. Most volatiles in this fraction followed a cubic (n=38) or quadratic model (n=14), which illustrates the complex physics occurring during distillation from the still.

The influence of compound volatility, affinity with water, and the interaction between the aroma volatile and the two solvents (ethanol and water) determined the elution of aroma volatiles throughout the hearts fraction of distillation.

Compounds with higher volatility (i.e. monoterpenes) were found in the earlier distillate samples in their highest concentrations through their preference to volatilise. Conversely, sesquiterpenes, sesquiterpenoids, and monoterpenoids were at their highest concentration in the later hearts distillate reflecting their lower volatility.

An enhanced understanding of the link between distillation time and volatile elution, highlights the rapidly changing flavour profile over the course of distillation, particularly in the hearts fraction. By understanding the elution of volatile compounds throughout distillation from the still, cut points may be adjusted to optimise specific characteristics.

Author Contributions

Hebe Parr: Visualisation, data curation, writing (original draft).
Rachel Sutherland: Conceptualisation, formal analysis, supervision, writing (review and editing).
Ian Fisk: Funding acquisition, supervision, conceptualisation, writing (review and editing).

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Conflict of interest

The authors declare that there are no conflicts of interest.

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