Research article

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Origins of the perceived nutty character of new-make malt whisky spirit

Emily Boothroyd,[1] Robert S. T. Linforth,[1] Frances Jack[2] and David J. Cook[1]*

New-make malt spirits were sourced from 35 individual Scotch Whisky distilleries and their sensory characteristics rated by a trained panel using descriptive analysis. Selected samples (either high or low in perceived nutty character) were analysed using gas chromatography–olfactometry to identify regions of the resulting chromatograms, and the underlying compounds that were associated with nutty, nutty–cereal or nutty–oily characters. The concentrations of 19 'candidate' nutty compounds were subsequently analysed in all 35 spirit samples and their analytical concentrations modelled as factors against sensory panel scores for 'nutty', 'oily', 'feinty' and 'cereal' characters. The model for spirit nutty character included positive contributions from 2,5-dimethylpyrazine, 2-furanmethanol and ethyl benzoate and a negative correlation with γ-nonalactone concentration. Analysis of a spirit sample manufactured using chocolate malt, and noted for its nutty character, confirmed the likely significance of pyrazine compounds to spirit nuttiness. Furfural concentration was positively correlated with perceived cereal, oily and feinty characters. Some co-correlation was evident between the four sensory characters, which may indicate that they have similar origins. Alternatively they may not be clearly defined from one another from a sensory perspective, or there might be complex interactions with other spirit flavours that mask or enhance these four attributes in a similar way. This highlights the likely complexity of nutty (and other Maillard related) characters in malt spirit. **Copyright © 2013 The Institute of Brewing & Distilling**

Keywords: malt whisky; new-make spirit; nutty aroma; Maillard reaction; distilling

Introduction

With annual exports over £3 billion, Scotch Whisky is by far the largest export earner in the UK food and drink sector. Nutty flavours are an important part of both mature whiskies and newly distilled malt spirit, as demonstrated by the presence of a 'nutty' category on the Scotch Whisky Flavour Wheel of the Scotch Whisky Research Institute (SWRI) *(1)*. However, the origins of these flavours are poorly understood. Lee *et al*. *(2)* used multivariate chemometric analyses to distinguish between the aroma characteristics of 40 blended Scotch whiskies, from 'deluxe' to 'multiple retailer' brands. Principal component analysis was used to determine the most significant sensory characteristics that discriminated between the whiskies; 'nutty' was one such example. Furthermore, both the 'nutty' and 'malty' attributes were considered to be characteristics mainly perceived in the deluxe blends, indicating that these particular features of whisky are highly regarded.

While nuttiness is a recognized sensory characteristic of new-make spirits, which is rated by trained sensory panels, the usage of the term 'nutty' may be poorly defined. In a recent investigation of the nutty sensory attribute across food categories, Miller *et al*. *(3)* identified five nutty concepts, which they found between them to adequately describe nuttiness across more than 200 food products. These were: 'overall nutty', 'nutty–beany', 'nutty–buttery', 'nutty–grain-like' and 'nutty–woody'. The fact that a single term was not adequate to describe the nutty attribute across these products hints at the complexity of this sensory term and the subdivisions arrived at in the research demonstrate that 'nutty' can take on differing characteristics in different food systems, which can be associated with oily character ('nutty–buttery'), cereal ('nutty grain-like'), woody or earthy ('nutty–beany') characteristics. Therefore, when a trained sensory panel scores 'nuttiness', what are they actually responding to in the spirit? Currently, the reference samples used to train panellists in this regard are spirit samples that exhibit the characteristic that has come to be known as 'nutty' within the industry.

It is informative to briefly consider some detailed studies that have explored the chemical origins of sensory nuttiness in other food systems. Tressl *et al*. *(4)* discussed lipid products and Maillard products, which they cited as compounds responsible for nutty flavours in malt. In particular, they attributed nuttiness to nitrogen heterocyclic compounds with either a five- or six-membered ring structure and varying side chains, including acetyl or alkyl groups. They noted the structural similarities between nutty aroma compounds and those responsible for cereal and bready aromas, which may be at the heart of some of the overlap of nuttiness with other sensory characters (e.g. nutty–cereal). These observations are highly significant to the present study, since they are based on the starting material for malt whisky manufacture.

* Correspondence to: David J. Cook, Brewing Science Section, Division of Food Sciences, The University of Nottingham, Sutton Bonington Campus, Loughborough, Leicestershire LE12 5RD, UK. E-mail: david.cook@nottingham.ac.uk

[1] Brewing Science Section, Division of Food Sciences, The University of Nottingham, Sutton Bonington Campus, Loughborough, Leicestershire LE12 5RD, UK

[2] The Scotch Whisky Research Institute, The Robertson Trust Building, Riccarton, Edinburgh EH14 4AP, UK

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Akiyama *et al.* *(5)* characterized the volatile compounds present during the grinding of roasted coffee beans. Four 'nutty–roast' compounds were recorded, of which three were pyrazines (heterocyclic nitrogen compounds). Avsar *et al.* *(6)* sought to determine the nutty flavour characteristics of young and matured cheddar cheeses. The extracts of cheeses, with and without nutty flavour, were analysed using dynamic headspace gas chromatography–olfactometry (GC-O). Of the five nutty flavour volatiles identified in the neutral/basic fraction of the nutty cheddar cheese extracts, four were pyrazines: tetramethylpyrazine ('nutty'), 2-isopropyl-3-methoxypyrazine ('dirty, nutty'), 2,3-diethyl-5-methylpyrazine ('sweet, nutty') and 2-isobutyl-3-methoxypyrazine ('nutty').

In a detailed investigation into the aromatic compounds of roasted cocoa, Bonvehi *(7)* was able to identify several nutty flavour compounds. Of the more than 100 aroma compounds identified in the study, eight were linked to nutty aroma characteristics, including pyrrole ('nutty, sweet'), 2-acetyl-5-methylfuran ('strong, nutty'), 2-acetylpyrrole and 2-acetyl-1-methylpyrrole ('bread, walnut, liquorice'), 2,3-diethylpyrazine ('nutty, hazelnut, cereal, meaty'), 3-hydroxy-2-methyl-4-pyrone and pyrrole-2-carboxaldehyde ('malt, roasted nuts'). From this list it is apparent that aroma compounds described as having nutty character are often also described as having cereal or malty characteristics.

In this paper, sensory and instrumental analyses were combined in order to better understand the origins of the nutty aroma character of new-make malt spirit. The potentially related sensory characters of 'cereal', 'oily' and 'feinty' aromas were also included in the study. The feinty character of malt whisky is a term used to describe the aroma of 'heavy', fusel compounds, which exit the still at the end of distillation, otherwise known as the feints.

In preliminary work *(8)*, five malt spirit samples were sourced from the industry, one of which was a 'non-nutty' control, while the other four had been scored by a trained sensory panel as exhibiting varying degrees of nuttiness. Aroma compounds were extracted from the spirit samples using both liquid–liquid extraction (LLE) and Solid Phase Extraction (SPE) methods. Gas chromatography–olfactometry of the extracts was used to identify regions of the chromatogram where odour descriptors relevant to the nutty percept were generated by panellists. The SPE method was then used to extract volatiles from 35 new-make spirit samples, sourced from distilleries across Scotland. Compounds that eluted in the 'nutty' related regions of the chromatograms were quantified in all 35 samples and their analytical concentrations were used to form predictive models for sensory panel scores of the spirits.

Materials and methods

Materials

Thirty-five new-make spirits, from malt whisky distilleries across Scotland, were supplied by the SWRI. These spirits represented typical industry production and exhibited a wide range of flavour characteristics. This set included the five spirit samples used in the preliminary GC-O work. One further more experimental spirit sample, with distinctive 'nutty' character, was also examined. This spirit had also been produced in a Scotch whisky distillery, but was manufactured using a significant proportion of chocolate malt in the grist.

Analysis of new-make spirit samples

Liquid–liquid extraction of aroma compounds. New-make spirit (100 mL) was spiked with an internal standard (2-acetylthiazole; 10 μg mL^{-1}), diluted with water (400 mL) and twice extracted with dichloromethane (200 mL). The two extracts were combined and concentrated to 1 mL under a stream of nitrogen.

Solid-phase extraction of aroma compounds. Spirit samples were extracted using a SPE method developed to selectively extract the relatively polar, hydrophilic aroma compounds present. It was considered that this selectivity would assist in the GC-O characterization of nutty spirit aromas in the presence of large concentrations of other bulk constituents of new-make spirit, such as ethyl esters. The method was adapted from the method of Ferreira *et al.* *(9)*, who had used a similar protocol to extract the highly polar compounds sotolon, maltol and furaneol from wine.

New-make spirit (5 mL) was diluted with water (25 mL). An internal standard was added (to achieve a concentration of 0.1 μg mL^{-1} 3-heptanone) and the mixture shaken, and allowed to equilibrate for a minimum of 4 h. LiChrolut EN SPE columns (Merck KGaA, Darmstadt, Germany; sorbent bed 500 mg) were placed on an SPE vacuum manifold (Phenomenex, Torrance, CA, USA), conditioned with 8 mL methanol and equilibrated with 8 mL aqueous ethanol (12% ABV). Spirit samples were loaded onto individual columns and allowed to fully saturate the sorbent bed for 1 min before a vacuum was applied. Once the sample had been loaded, care was taken not to allow the bed to run dry until after the wash step, during which water (5 mL) was run through the cartridge. The sorbent bed was then dried by applying a vacuum (10 kPa) for 30 min. Aroma compounds were eluted from the cartridge into dichloromethane (6 mL). Each spirit sample was thus extracted in triplicate and in a randomized order. Dichloromethane extracts were dried with anhydrous magnesium sulphate (Sigma Aldrich; Poole, Dorset, UK) and concentrated to a final volume of 1 mL under a stream of nitrogen prior to analysis.

GC-MS analysis of spirit extracts. Aroma extracts in dichloromethane were analysed using a ThermoScientific Trace GC Ultra with a DSQ II mass spectrometer and an AS 3000 Autosampler (Thermo Electron Corporation). Compounds were separated on a Zebron ZB-WAX column (30 m × 0.25 mm i.d., 1.0 μm film thickness; Phenomenex, Macclesfield, UK) starting at an oven temperature of 40 °C (1 min hold) followed by a ramp to 250 °C at 8 °C min^{-1}. The helium carrier gas flow rate was 1.5 mL min^{-1} and injection (1 μL; temperature 240 °C) was splitless. The transfer line from the oven to the mass spectrometer was maintained at 250 °C. The mass spectrometer was operated in full scan mode over the range *m/z* 35–250.

Identification and quantitation of compounds was achieved using the Qual and Quan Browser applications of Xcalibur Software (Thermo Electron Corporation, Altrincham, Cheshire, UK). Identification was based upon: (a) EI-MS library matching; (b) measurement and confirmation against literature sources of the linear retention index (LRI) against alkanes; and, where possible, (c) confirmation of the retention time of an authentic standard run under identical chromatographic conditions.

Compound concentrations were calculated following normalization to the internal standard (0.1 μg mL^{-1} 3-heptanone) and where possible, the use of individual relative response factors calculated from injection of external standard solutions of

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known concentration. The authentic external standards used for calibrations (all >99% purity) were: 2-furanmethanol, furfural, 2-methylpyrazine, 2,5-dimethylpyrazine, ethyl octanoate, benzaldehyde and 1-octen-3-ol.

GC-O of spirit extracts. A subset of five new-make spirit samples, of known and varying degrees of nutty character, were used for GC-O investigation. Sample extracts (LLE and SPE) were analysed by GC-O to identify the key odour active regions of the chromatogram with nutty or cereal related odour characteristics. Because of the complexity of 'nuttiness' as a sensory attribute, the range of sensory descriptors deemed as relevant was quite varied, for example, including nutty related characteristics like 'oily' or 'cereal'.

A splitter was fitted to the end of the ZB-WAX column (30 m × 0.25 mm i.d., 1.0 μm film thickness; Phenomenex, Macclesfield, UK), such that approximately half of the flow was diverted to an 'odour sniffing port' via a fused silica capillary passing within a heated transfer line, set at a temperature of 180 °C. In preliminary GC-O runs, the oven temperature ramp of 8 °C min^{-1} was deemed too fast to distinguish between odours, therefore 4 °C min^{-1} was used instead. As the runs were 52 min long, two assessors were used to sniff each chromatogram, swapping over half-way, in order to avoid fatigue. Each panellist undertook two GC-O assessments of each spirit sample. Assessors were asked to record the retention time at which they perceived an odour, an appropriate descriptor, the intensity of that odour (on a scale of 1–3) and its duration. These data were recorded on paper under the relevant column headings. A panel of seven assessors (five male, two female, between 20 and 50 years of age) were used for the GC-O work. They were members of the flavour research group, experienced in the task of conducting GC-O, but were given no prior knowledge of the nature of the samples they were sniffing, or of the kind of odours to expect.

Sensory evaluation. The aromas of the 35 spirit samples were assessed by the SWRI's expert sensory panel, which has extensive experience in the evaluation of whiskies and associated spirits. The samples were diluted to 20% ABV and 30 ml presented in clear nosing glasses, covered with watch glasses. Panellists were asked to score the intensities of 'nutty', 'cereal', 'oily' and 'feinty' aromas in each sample, using a scale of 0–3. The panel has previously been trained to recognize these attributes using a range of production samples, spirit with the key flavour characters and, where available, individual flavour compounds. The sensory assessments were carried out over a number of sessions, with a minimum of 10 panellists participating in each session. Mean panel scores were calculated for each attribute.

Table 1. Gas chromatography–olfactometry (GC-O) identification details and mean concentrations of 19 volatile compounds analysed across 35 new-make spirit samples. Sixteen of these compounds were in regions of GC-O chromatograms associated with 'nutty/cereal' aroma descriptors; the remaining three were long-chain ethyl esters, which were included in the modelling of spirit sensory characters

GC-O descriptors in chromatogram region	Main peak(s) (quantitatively) in chromatogram region	Linear retention index (LRI) (ZB-Wax; alkanes)	Mean (±SD) concentration across 35 spirit samples (μg mL^{-1})
Malty, solvent, fruity, floral, nuts, chocolate, alcohol	Ethyl butyrate	1055	2.29 ± 0.74
Malty, alcoholic, solventy, nutty, almond/marzipan biscuit	Pentan-1-ol	1263	6.96 ± 1.76
	thiazole	1286	0.36 ± 0.09
	2-Methyl pyrazine	1297	0.08 ± 0.03
Roasted, nutty popcorn, nutty baked, savoury	2,5-Dimethylpyrazine	1353	0.04 ± 0.03
Oily, faecal, sulphury, nutty/roasted, nut, caramel, meaty sulphur	2-Nonanone	1412	1.14 ± 0.50
Roasted, warm barley, walnut, popcorn, nutty, mushrooms/oily	1-Octen-3-ol	1461	0.84 ± 0.21
Malt/maltesers, savoury, baked, oaty, oily, peanuts, fatty roasted/burnt, nutty.	Furfural	1498	12.4 ± 4.4
Raw nut, snickers, green vegetable, earthy, nutty	2-Acetylfuran	1542	1.40 ± 0.67
Feints, aldehyde, marzipan/almond, solvent, oily, solventy, sweet	Benzaldehyde	1575	0.33 ± 0.11
Cucumber, green, mint, metal, floral, nutty, green leaves, onion, mossy/peaty, coconut	5-Methylfurfural	1612	0.80 ± 0.28
—	Ethyl decanoate	1663	77.0 ± 29.5
Popcorn, socks/musty, earthy, feet	2-Furanmethanol	1682	0.69 ± 0.25
Beefy, yeast extract, savoury, nutty, earthy, malty, oily, aldehyde	Ethyl benzoate	1708	2.47 ± 1.15
Yeasty, baking, green, malt/wheat, potato,	Methionol	1746	0.53 ± 0.28
—	Ethyl dodecanoate	1869	52.5 ± 23.2
Chestnuts, cake, almond, cinnamon	2-Phenethyl alcohol	1961	680.46 ± 191.70
Sweet/popcorn/caramel, waxy/coconut	γ-Nonalactone	2088	1.35 ± 0.60
—	Ethyl hexadecanoate	2198	2.95 ± 1.16

Analytical data are the mean of three replicate determinations for each spirit sample.

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Modelling of sensory data versus new-make spirit aroma composition

Data were entered into experimental design software (Design Expert, version 7.0, Stat-Ease, MN, USA) using a D-optimal factorial design space. The mean panel scores for each of the 35 spirit samples for oily, nutty, cereal and feinty characters were entered as four responses, each of which was modelled against 19 factors, which were the analytical concentrations of the compounds listed in Table 1. Modelling proceeded via progressive factor reduction, successively removing the factors that were of least significance in derived models, until a significant model resulted with factors, each of which were significant ($p < 0.05$), and the model R^2 was maximized.

Results and discussion

GC-O

Identification of an 'odour active region' was based upon the frequency and/or intensity of aroma reported at a particular retention time. Using LLE of aroma compounds, 17 odour active regions were identified on the resulting GC-O chromatograms with descriptors related to either nutty, nutty–cereal or nutty–oily percepts. However, when using the SPE extraction technique, this was increased to 23. This may simply have reflected variation in the efficiency of the panel in generating the relevant descriptors in each experiment. However, we believe it was most likely a result of the increased selectivity of the LiChrolut EN cartridges for the aroma compounds responsible for nutty/cereal aroma characteristics. The SPE clean-up technique did not increase the recovered concentrations of many compounds. However, it significantly reduced the concentrations of interfering compounds in new-make spirit, which were present at a high concentration, but which did not contribute to nutty aroma.

The GC-O descriptors generated (Table 1) varied widely, with both compound and assessor. It should be noted that, while the GC separation was optimized as much as possible, the constraints of overall run time on assessor fatigue, coupled with the complex mixture of volatile compounds in new-make spirit, meant that inevitably not all aromas and their underlying peaks were fully separated. This is apparent from inspection of the odour descriptors in Table 1, where quite diverse sensory descriptors (e.g. oily, faecal, sulphury, nutty/roasted, nut, caramel, meaty sulphur) were noted in the same chromatogram region and appear to result from the presence of at least two odour active compounds (i.e. a meaty/sulphury/faecal compound and a nutty/roasted/caramel compound). Furthermore, neither aroma grouping fits comfortably with the known aroma properties of the quantitatively significant peak in that region of the chromatogram, 2-nonanone ('hot milk', 'waxy', 'green'). The 19 compounds listed in Table 1 were the compounds selected for modelling against sensory data. Of these, 16 were selected because they were quantitatively the major peaks in chromatogram regions where strong nutty/cereal/oily odours were consistently reported by the panel. The remaining three compounds were ethyl esters of varying chain length, which were included in the model owing to prior interest in the physicochemical impacts of long-chain ethyl esters on the partitioning behaviour of aroma compounds in malt spirits *(10)*.

Modelling sensory data against analytical concentrations of 'candidate' compounds

The mean panel scores for each rated attribute of the 35 spirits are shown in Table 2. The quantitatively predominant compounds in each of the nutty/cereal odour active regions of the SPE chromatograms were considered to be 'candidate' nutty/cereal congeners. However, it is acknowledged that underlying 'trace' peaks, with low odour thresholds, are most likely responsible for some of the 'inconsistent' aromas noted against the compounds listed in Table 1. Concentrations of each candidate peak were analysed in triplicate for all 35 spirit samples and the mean congener concentrations were then modelled against sensory scores for spirit 'nutty', 'cereal', 'oily' and 'feinty' characters. Congener concentrations were treated as factors in a D-optimal experimental design space, against which the sensory scores were modelled, using Design Expert version 7. Successive factor elimination was used to reduce the number of model factors, until the model R^2 value was maximized, and all model factors were

Table 2. Mean sensory panel scores for feinty, cereal, nutty and oily aromas in the 35 new-make spirit samples

Spirit sample	Feinty score	Cereal score	Nutty score	Oily score
1	0.77	0.45	0.26	0.63
2	0.97	0.96	0.38	0.54
3	1.30	0.99	0.61	0.66
4	0.72	0.61	0.52	0.55
5	0.94	0.48	0.35	0.67
6	1.16	0.95	0.45	0.80
7	1.08	0.60	0.57	0.66
8	1.28	0.84	0.74	0.95
9	0.94	0.68	0.31	0.77
10	0.83	0.62	0.38	0.71
11	0.94	1.12	0.58	0.94
12	1.06	0.53	0.62	0.70
13	0.77	0.51	0.42	0.81
14	1.03	0.91	0.66	0.95
15	1.15	0.79	0.35	0.79
16	1.16	0.95	0.51	1.10
17	1.26	0.88	0.35	0.99
18	0.98	0.82	0.55	0.73
19	1.06	0.86	0.48	0.75
20	0.66	0.55	0.17	0.49
21	0.78	0.55	0.25	0.58
22	0.74	0.41	0.29	0.57
23	1.51	1.11	0.65	1.27
24	1.64	1.31	0.78	1.25
25	1.63	1.18	0.54	1.07
26	1.36	1.12	0.65	1.04
27	1.20	1.10	0.82	0.92
28	1.10	0.88	0.94	0.89
29	1.29	0.94	0.72	0.80
30	1.04	0.76	0.69	0.85
31	0.69	0.37	0.51	0.54
32	1.52	1.17	0.58	0.70
33	0.73	0.69	0.22	0.75
34	0.95	0.75	0.62	1.09
35	1.09	0.97	0.88	0.98

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significant at the 95% level ($p < 0.05$). The significant model terms for sensory 'nutty', 'cereal', 'oily' and 'feinty' scores are summarized in Table 3. Where a compound was a significant factor in a model, the quoted p-value indicates the significance of the factor ($p < 0.05$) and the '±' indicates the directionality of the impact on the perceived sensory character; for example, 2,5-dimethyl pyrazine was a significant factor in the model for perceived spirit nuttiness ($p = 0.0003$) and increasing concentrations of the compound increased perceived nuttiness (+, positive correlation).

Before continuing to discuss the significant factors in each model (Table 3), it is worth noting that significance of a term in such models only implies that a significant correlation was observed in the dataset ($n = 35$); clearly this does not confirm that there was a causal relationship between the factor (aroma compound) and the particular sensory characteristic – they might simply have co-varied over the design space. The origin of effects in such studies can be complex, particularly since perceived aroma characters in products such as whisky usually result from the interaction of multiple compounds.

The model for the nutty character of new-make spirit included the concentrations of 2,5-dimethylpyrazine, 2-furanmethanol and ethyl benzoate as significant factors that correlated positively with perceived nuttiness, while γ-nonalactone had a negative impact on sensory nuttiness (Table 3). The compound 2,5-dimethylpyrazine has been reported to contribute to nutty odours in other food systems *(7,11,12)*, which is consistent with the current finding. The compound 2,5-dimethylpyrazine was also a positive factor in the model for perceived oiliness of the spirits; it is interesting to note this crossover between the linked concepts of nutty and oily.

The compound 2-furanmethanol is a Maillard reaction product with a 'burnt' sensory character, which could feasibly be associated with a roasted dimension to perceived nuttiness. Alternatively, it is possible that 2-furanmethanol concentrations in the spirit samples are a marker of the extent of other Maillard products present and that some of those other compounds specifically contribute nutty character. Ethyl benzoate is not a compound usually associated with nuttiness in foods and beverages. Its character has been described as floral, fruity or celery-like. The compound γ-nonalactone is the main constituent of synthetic coconut aroma. The negative correlation here is counterintuitive and difficult to explain. However, it would appear that this coconut character is distinct from the character scored as nutty in whisky, to the extent that it may mask or detract from the perception of spirit nuttiness.

The models for the other spirit aroma characteristics (cereal, oily and feinty), share some common features – namely that furfural concentrations correlated positively with each character, whereas γ-nonalactone had a negative impact on these sensory scores, similar to the impact noted above for the sensory nutty character. When the sensory scores for cereal, oily and feinty were plotted against sensory nuttiness (Fig. 1), it was apparent that there were weak co-correlations between these sensory characters. In the case of nutty–cereal and nutty–oily, this overlap is consistent with reports of nutty percepts from other studies *(3)*. The feinty character of whisky, like nuttiness, may be poorly defined and have complex origins, since it is a character

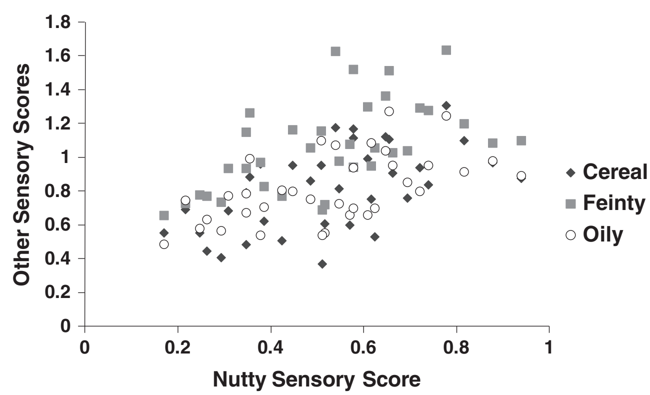

Figure 1. A scatter plot indicating the positive co-correlations between the nutty character of new-make spirit and cereal, feinty and oily characters (mean sensory intensity data for 35 spirit samples, $n = 13$).

Table 3. Aroma compounds, analytical concentrations of which were found to be significant factors in models derived to predict the 'nutty', 'cereal', 'oily' or 'feinty' characters of new-make spirit. Where a compound was a significant factor, the quoted p-value indicates the significance of the factor ($p < 0.05$) and the '±' indicates the directionality of the impact on the perceived sensory character

	Model for sensory data			
Aroma compound	Nutty	Cereal	Oily	Feinty
Pentan-1-ol	—	0.0169+	—	0.0031+
Thiazole	—	0.0037−	—	—
2,5-Dimethylpyrazine	0.0003+		0.0004+	—
2-Nonanone	—	—	0.0246−	—
Furfural	—	0.0098+	0.0008+	<0.001+
2-Acetylfuran	—	0.0018+	—	
Benzaldehyde	—	—	—	0.0021−
Ethyl decanoate	—	0.0371−	—	<0.0001−
2-Furanmethanol	0.0007+	—	—	—
Ethyl benzoate	0.0234+	—	—	—
γ-Nonalactone	0.0003−	0.0024−	<0.0001−	0.032−
Model R^2	0.57	0.53	0.55	0.66
Model significance (probability > F)	<0.0001	0.0003	<0.0001	<0.0001

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Table 4. Heterocyclic nitrogen compounds identified in extracts of a particularly 'nutty' malt spirit manufactured using chocolate malt

Compound	LRI (experimental) ZB-Wax	LRI (literature)[a]	Aroma descriptors
2-Methylpyrazine	1297	1288	Nutty, popcorn[b]
2,5-Dimethylpyrazine	1353	1347	Roasted nut[b]
2-Ethyl,6-methylpyrazine	1415	1411	Roast potato, roast hazelnut[c]
2-Ethyl,5-methylpyrazine	1422	1419	Coffee, nutty
2-Ethyl-3-methylpyrazine	1435	1432	Nutty, peanut, musty[c]
2,6-Diethylpyrazine	1464	1463	Nutty, hazelnut[c]
3-Ethyl-2,5-dimethylpyrazine	1473	1474	Burnt, popcorn[b]

Compound identification was on the basis of EI-mass spectrum library matching and by comparison of the experimental linear retention index (relative to alkanes) as compared with literature values for ZB-Wax or similar phase columns.
[a]Sanz et al. *(19)* working with an HP-Wax column (60 m × 0.25 mm × 0.5 μm film thickness).
[b]www.flavornet.org
[c]http://www.thegoodscentscompany.com

associated with the final cut-point for spirit collection and as such will be associated with less readily distilled components of various chemical natures. The correlation here with nutty character may indicate that the compounds responsible for nutty character have similar volatilities to those responsible for feinty character, that is, be late distilling. The true markers of feinty character may not have been included in the present study because the candidate compounds were selected based on GC-O work focused on nutty/cereal or nutty/oily characters. However, the derived model for feinty character was significant and had an R^2 value of 0.66, suggesting that this character was correlated positively with pentan-1-ol and furfural spirit concentrations. The compounds that had a negative impact on feinty character (benzaldehyde, ethyl decanoate, γ-nonalactone) may be those that mask feinty character to some extent.

Analysis of a highly nutty new-make spirit manufactured using chocolate malt

The final spirit analysed in this study was produced using a significant proportion of chocolate malt and was of particular interest owing to its distinctive nutty character. Chocolate malt is a roasted malt product, which is manufactured by heating pale malt in a roasting drum at temperatures up to around 230 °C *(13)*. This process generates many volatile flavour compounds as a result of Maillard reaction chemistry *(14,15)*. In particular, at these high finishing temperatures, heterocyclic nitrogen and sulphur compounds are formed, giving the product an aroma somewhat similar to roasted coffee or cocoa beans *(16)*.

GC-MS analysis of the chocolate malt spirit identified that it contained a number of compounds that were either absent, or present at lower levels, in the 35 standard new-make spirit samples. Table 4 lists the compounds identified in the chocolate malt spirit extract and which eluted at retention indices that coincided with the use of nutty related descriptors by the GC-O panel as reported in Table 1. These compounds are all pyrazines, only two of which (2-methylpyrazine and 2,5-dimethylpyazine) were present at sufficient quantities in the 35 standard spirit samples to have been routinely analysed and used as factors in the modelling experiment. We consider that some of the nutty odour descriptors reported by panellists in the GC-O work (Table 1) most likely originated from pyrazine compounds, underlying the quantitatively prevalent compounds listed in Table 1. For example, the nutty aromas in the region of 2-nonanone (Table 1, LRI 1412) could have originated from trace levels of 2-ethyl-6-methylpyrazine (LRI 1415) or its positional isomers (2-ethyl-5-methylpyrazine, LRI 1422; 2-ethyl-3-methylpyrazine, LRI 1435). Ethyl-methylpyrazines (LRI range 1415–1435) are associated with roast, nutty and toffee-like odours *(17)* and have much lower odour thresholds than their dimethyl counterparts, hence they are likely to have an impact on overall aroma even when present in trace amounts *(18)*. Similarly, 1-octen-3-ol (LRI 1460) was responsible for the mushroom-like aroma reported during GC-O (Table 1), yet the nutty notes reported by several panellists simultaneously now seem likely to have been contributed by 2,6-diethylpyrazine (LRI 1464; 'hazelnut') or 3-ethyl, 2,5-dimethylpyrazine (LRI 1473; 'potato, roast'*(19)*).

Conclusions

Nutty and cereal characters of whisky are of complex origin and probably derive from the presence of multiple congeners in a synergistic mixture. Work presented here supports the view that nitrogen heterocyclic compounds, and in particular pyrazines, play an important role in the perceived nutty character of new-make malt spirit. Not all of the compounds that were associated with nutty regions of the GC-O chromatograms were found to be correlated with sensory panel scores for nuttiness, or the related characters of oily and cereal. In some chromatogram regions, the quantitatively significant compounds were unlikely candidates to be the source of nutty aromas. However, their presence hindered attempts to sensitively analyse low levels of co-eluting compounds with low odour thresholds. Furthermore, some compounds (e.g. 2-furanmethanol), whose analytical concentrations correlated positively with spirit nuttiness, may make synergistic contributions to spirit nutty character. Alternatively, they could be markers of, and co-vary with, the levels of other Maillard products (such as pyrazines), which actually determine the perceived nutty intensity.

The nutty aroma of whisky is a complex sensory character, both because its congeners are linked to the production of families of compounds generated via Maillard reaction pathways and because the nutty percept has crossover into related characters such as 'cereal' or 'oily'. In separate publications, we have demonstrated that wash lipid levels *(20)* and the analytical concentrations of long-chain esters *(10)* also appear to play a part in

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the perceived nuttiness of spirits. High wash lipid levels change the Maillard reaction product spectrum generated during distilling and enhance certain compounds that emphasize the nutty–oily character, categorized as nutty–buttery by Miller *et al*. *(3)*. The impact of long-chain esters *(10)* was concluded to be a physicochemical effect, whereby the formation of agglomerates at high concentrations selectively incorporates hydrophobic aroma compounds. This results in an increased 'emphasis' of the sensory character of relatively polar, hydrophilic compounds (such as pyrazines) in the whisky headspace. The emerging picture is a complex one, but suggests routes by which process control of nuttiness might be enhanced and offers an improved understanding of the sensory nature of perceived nuttiness in malt spirits and the corresponding mature whisky.

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