Origins of Flavour in Whiskies and a Revised Flavour Wheel: a Review

By K.-Y. Monica Lee, Alistair Paterson* and John R. Piggott

Centre for Food Quality, University of Strathclyde, Department of Bioscience, 204 George Street, Glasgow G1 1XW, Scotland, UK

and

Graeme D. Richardson

The Scotch Whisky Research Institute, The Robertson Trust Building, Science Park North, Riccarton, Edinburgh EH14 4AP, Scotland, UK

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The nature and origins of flavour in whiskies are reviewed with the aim of developing a revised and simplified flavour wheel for training of sensory assessors. Scotch whiskies are perceived as having distinctive characters, generally recognised in pattern recognition (perception, macroscopic brain processing), rather than being subjected to a deconstruction process of evaluating attributes (sensation, microscopic brain processing). Although consumers use simple recognition judgements on whisky flavour in categorical assimilation, industry has a requirement for monitoring spirit quality that necessitates a more reductionist approach. Whisky flavour wheels identify attributes, specific components of flavour character, which can be demonstrated to sensory assessors using reference standards. The advent of cyclodextrin bound reference standards has enabled communication of information on flavour character in training of assessors, as exploited in the brewing industry. A revised flavour wheel, with characters illustrated by reference standards, is proposed to assist sensory training on attributes of whisky flavour character.

Key Words: Whisky flavour character, whisky flavour reference standards, flavour perception and sensation, sensory assessor training, quality evaluation.

INTRODUCTION

Appreciation of whisky character is a synergistic and holistic perceptual process with extrinsic attributes: Improved congener analyses have not yielded greater understanding of whisky flavour5; a dynamic interaction229 between individuals and flavour components208. Perceptions of flavour notes or attributes can be expressed as language209,233 but are more commonly used in Gestalt45,91,107,161,232,242 or holistic pattern recognitions in human brains221, perception of whole over parts (macroscopic brain processing) (Fig. 1)107,242. In contrast, in industrial sensory assessments, quantified sensations are integrated from specific groups of olfactory receptors (microscopic processing). Assessors can also agree on character while differing in quantities of mouth-space volatile flavour components135.

In consumers, causality interactions (slaving effects) exist between perceptual and sensation levels, dictated by cues117 (Fig. 1): the human mind influences the brain242.

*Corresponding author
INTRINSIC ATTRIBUTES

Appearance,
Aroma,
Taste,
Mouthfeel,
Aftertaste

EXTRINSIC ATTRIBUTES

Expectation,
Experience,
Brand Image,
Packaging,
Marketing,
Price

Sensation

Microscopic level

Perception

Macroscopic level

FIG. 1. Intrinsic and extrinsic attributes.

in long-term memory. Spatial response patterns of flavour component mixtures may thus not be summations of individual flavour notes.

The beer flavour wheels concentrate assessor attention to specific flavour attributes, including mouthfeel attributes, important in beer. Studies of wood-matured ports and whisky suggest expert and novice assessors judge flavour character from visual data (slaving effect), a feature common in humans. Manipulating appearance changes perceptions of product character - aroma, taste and flavour. Processes of odour recognition involve primary visual cortex (BA17) activity, involving comestibility (suitability for drinking) of products.

Flavour wheel presentations of whisky attributes serve useful functions in directing attention towards specific features of character, forming bases for discussions through definition of vocabularies. Specific reference standards facilitate conceptualisations (knowing an attribute) and development of parallel mental representations of concepts, important in assessor training (ISO 8586-1:1993, 8586-2:1994). Visual representation or symbols could aid recognition or memory and assessor training.

WHISKY MATURATION

Ageing new distillates in oak yields mature whisky. This process, central to whisky character development, gives consumer appeal. Maturing can be considered replacement of pungent, soapy, sour and harsh notes in new distillates with smooth, matured and mellowness attributes. Such judgements also employ pattern recognition with collections of stimuli from sensory systems (visual, olfactory, gustatory and chemesthesia), integrating in specific brain regions to form macroscopic representations of whiskies (Fig. 1).

Research on model and malt whiskies suggests wood maturations change partitioning of key flavour components with less desirable flavour notes, increasing retention in liquid phases, recently simulated.

Fatty acid ethyl esters, amphiphiles with central polar groups and peripheral hydrophobic aliphatic carbon chains, are important in stabilising whisky headspace compositions. Structure influences solubility in aqueous ethanol: excess esters form agglomerates, yielding microemulsions. At 23% (abv), agglomerate diameters increase forming hazes. Chill filtration, prior to bottling, removes excess agglomerates - changing congener composition but not sensory quality. Agglomerates are dominated by ethyl dodecanoate, tetradecanoate, hexadecanoate, contributions determined by aliphatic chain length. Other congeners - alcohols, aldehydes and acids - also contribute to agglomerates, influencing sensory character.

In wood maturations, non-volatile components, including sterols and tannic acids, stabilise ester agglomerates. Temperature influences both agglomerate behaviour and distribution of flavour-active congeners between solution and headspace phases. At oral temperatures, agglomerates suppress volatile congeners more efficiently, but differences between nosing and tasting are thought generally small. In summary, in agglomerate formation congener activity coefficients are increased by extracted wood components.

In summary, in agglomerate formation congener activity coefficients are increased by extracted wood components. Alcohol strength influences congener distribution and spirit matrix structures. Below 20% abv, ethanol
molecules are mono-dispersed in water; between 20 and 57% abv, ethanol molecules progressive aggregate to reduce alkyl chain hydrophobic hydration and above 57% abv, solutions are ethanolic with loss of water hydrogen-bonded networks. Increasing ethanol concentration lowers interfacial tension between aqueous phases and ethyl esters, increasing aroma thresholds. Reducing bottling strength (40% to 30-35% abv) increases headspace partition coefficients, decreasing aroma thresholds influencing longer-chain soap-like esters. Bottling strength thus influences perceived spirit quality. Dilution of a whisky to 23% abv maximises volatile release from distillates, optimising sensory assessment.

WHISKY PRODUCTION

Malt, grain and blended Scotch whiskies differ in production process (Fig. 2). In malt whiskies (4% market sale by volume – UK Food & Drinks Report, 1999) parameters in batch (pot) distillations of washes from barley malts influence final character. Grain whisky is a product of continuous fractional distillation of fermented wheat and maize, saccharified by lightly-kilned barley malts. Dominant (90% market) are blends of grain (60–80%) and malt (20–40%) whiskies with lighter grain (2–3) providing a flavour background, and single malts (up to 40) the majority of character. Selection of primary (top-dressing) and secondary malts has significant impacts. Maturations influence final flavour in blends or single whiskies with cask management ensuring product consistency.

A REVISED WHISKY FLAVOUR WHEEL FOR SENSORY ANALYSIS

The flavour wheel of Shortreed and coworkers ordered attributes in classifications based on production.

FIG. 2. Production of Scotch whisky.
FIG. 3. Revised Scotch whisky flavour wheel for industrial purposes.
<table>
<thead>
<tr>
<th>Code</th>
<th>Flavour Wheel term</th>
<th>Reference compounds for assessor training</th>
<th>Concentration (mg litre⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N.1</td>
<td>Pungent</td>
<td>Formic acid</td>
<td>10 x 10⁻¹</td>
</tr>
<tr>
<td>A.1.2</td>
<td>Burnt smoky</td>
<td>Guaiacol</td>
<td>27</td>
</tr>
<tr>
<td>A.3</td>
<td>Medicinal</td>
<td>α-Cresol</td>
<td>1.75</td>
</tr>
<tr>
<td>B.2</td>
<td>Malty</td>
<td>Malted barley</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2- and 3-Methyl butanal</td>
<td>0.6 (2-methyl butanal)</td>
</tr>
<tr>
<td></td>
<td></td>
<td>4-Hydroxy-3-(or 5) -ethyl-2(or 5)-methyl-3(2H) furanone</td>
<td>1.25 (3-methyl butanal)</td>
</tr>
<tr>
<td>C.1</td>
<td>Grassy</td>
<td>Hexanal</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>cis-3-Hexene-1-ol</td>
<td>1.00 x 10⁻³</td>
</tr>
<tr>
<td>D.1</td>
<td>Solventy</td>
<td>Ethyl acetate</td>
<td>1.12 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>2-Methyl propan-1-ol</td>
<td>1.00 x 10⁻³</td>
</tr>
<tr>
<td>D.2</td>
<td>Fruity (apple)</td>
<td>Ethyl hexanoate</td>
<td>2</td>
</tr>
<tr>
<td>D.3</td>
<td>Fruity (banana, pear-drop)</td>
<td>isoAmyl acetate</td>
<td>7</td>
</tr>
<tr>
<td>D.5</td>
<td>Berry</td>
<td>Thiomenthone</td>
<td>3 x 10⁻¹</td>
</tr>
<tr>
<td></td>
<td>Catty</td>
<td>Thiomenthone</td>
<td>1.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Sodium sulfide · mesityl oxide</td>
<td>100 each</td>
</tr>
<tr>
<td>E.1</td>
<td>Floral (Natural - rose) - violet</td>
<td>Phenyl ethanol</td>
<td>1.52 x 10⁻³</td>
</tr>
<tr>
<td></td>
<td>Floral (Artificial - scented, perfumed)</td>
<td>α-, β-Ionone</td>
<td>&gt;3x10⁻³</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Geraniol</td>
<td>19</td>
</tr>
<tr>
<td>G.5</td>
<td>Nutty (coconut)</td>
<td>Whisky lactone</td>
<td>266</td>
</tr>
<tr>
<td></td>
<td>Marzipan</td>
<td>Furfural</td>
<td>839</td>
</tr>
<tr>
<td>G.6</td>
<td>Vanilla</td>
<td>Vanillin</td>
<td>43</td>
</tr>
<tr>
<td>G.7</td>
<td>Spicy</td>
<td>4-Vinyl guaiacol</td>
<td>71</td>
</tr>
<tr>
<td></td>
<td>Spicy (clove)</td>
<td>Eugenol</td>
<td>1 - 55</td>
</tr>
<tr>
<td>G.8</td>
<td>Caramel (candy floss)</td>
<td>Maltol</td>
<td>1.14 x 10⁻³</td>
</tr>
<tr>
<td>G.10</td>
<td>Mothball</td>
<td>Naphthalene</td>
<td>&gt;8x10⁻³</td>
</tr>
</tbody>
</table>
2.4,6-Trichloroanisole \( \text{K} \)
Geosmin, 2-methyl \( \text{iso} \)-borneol \( \text{J} \)
Acetic acid \( \text{I} \)
2-Nonenal \( \text{M} \)
Dimethyl tri-sulphide (DMTS) \( \text{J} \)
Hydrogen sulphide \( \text{H}_2\text{S} \)
Methyl (2-methyl-3-furyl) disulphides \( \text{J} \)
Hydrogen sulphide \( \text{I} \)
Acetaldehyde \( \text{L} \)
Ethyl laurate \( \text{L} \)
Butyric acid \( \text{L} \)
Diacetyl \( \text{L} \)

<table>
<thead>
<tr>
<th>G.11</th>
<th>Mouldy</th>
<th>2.4,6-Trichloroanisole ( \text{K} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>G.12</td>
<td>Earthy, musty</td>
<td>Geosmin, 2-methyl ( \text{iso} )-borneol ( \text{J} )</td>
</tr>
<tr>
<td>J.1</td>
<td>Vinegary</td>
<td>Acetic acid ( \text{I} )</td>
</tr>
<tr>
<td>J.1.6</td>
<td>Cardboard</td>
<td>2-Nonenal ( \text{M} )</td>
</tr>
<tr>
<td>J.2</td>
<td>Stagnant, rubbery</td>
<td>Dimethyl tri-sulphide (DMTS) ( \text{J} )</td>
</tr>
<tr>
<td>J.3</td>
<td>Yeasty</td>
<td>Hydrogen sulphide ( \text{H}_2\text{S} )</td>
</tr>
<tr>
<td>J.5</td>
<td>Rotten egg</td>
<td>Hydrogen sulphide ( \text{I} )</td>
</tr>
<tr>
<td>J.6</td>
<td>Meaty</td>
<td>Methyl (2-methyl-3-furyl) disulphides ( \text{J} )</td>
</tr>
<tr>
<td>J.7</td>
<td>Vegetable (sweet corn, cooked cabbage)</td>
<td>Dimethyl sulphide (DMS) ( \text{J} )</td>
</tr>
<tr>
<td>J.8</td>
<td>Gassy</td>
<td>Ethanethiol ( \text{J} )</td>
</tr>
<tr>
<td>k.1</td>
<td>Yeasty</td>
<td>n-Butyric acid/ethyl butyrate ( \text{L} )</td>
</tr>
<tr>
<td>k.2</td>
<td>Rancid</td>
<td>\text{iso}-Valeric acid ( \text{L} )</td>
</tr>
<tr>
<td>L.1</td>
<td>Oily</td>
<td>Heptanol ( \text{L} )</td>
</tr>
<tr>
<td>L.2</td>
<td>Soapy</td>
<td>Ethyl laurate ( \text{L} )</td>
</tr>
<tr>
<td>L.3</td>
<td>Buttery</td>
<td>1-Decanol ( \text{L} )</td>
</tr>
<tr>
<td>L.4</td>
<td>Vegetal</td>
<td>Diacetyl ( \text{L} )</td>
</tr>
</tbody>
</table>

| <10 | 10 | \( 5.32 \times 10^3 \) |
| <1 | 1 | \( 0.08 \) |
| <3 | 3 | \( 0.02 \) |
| <7 | 7 | \( 0.14 \) |
| <0.6 | 0.6 | \( >7.2 \times 10^4 \) |
| <2 | 2 | \( >2 \) |
| <1 | 1 | \( >100 \) |
| <0.1 | 0.1 | \( >100 \) |

Hybrid structures considering production and flavour perception are more likely to be of industrial value. The revised whisky flavour wheel (Fig. 3), similar to other alcoholic drinks\(^{317,379}\), has a hierarchy of three tiers: primary — production origin or generality of nature; secondary — specific sensory or conceptual descriptors; and tertiary — highly specific terms, certain of technical importance. Attributes, in clockwise order, are on the right arising in normal production suitable for promotional and marketing purposes. On the left, off-notes, for technical functions, form four groups.

In the revision, primary tier chemical terms (phenolic, aldehydic, estery) were substituted with common industrial terms (peaty/smoky, grassy, fruity and floral, respectively). The generic feints\(^{141}\) was not replaced as of industrial value. Blenders and sensory assessors in Scotch whisky\(^{129}\) more often use subtier terms. For assessor training, reference compounds are recommended (Table 1): formulations with cycloextrins achieve consistency and parallel conceptualisations.

### Nasal effects

**N.1.** Pungency — ethanolic, peppery, prickle

**N.2.** Drying

Pungency, a primary common chemical sense (irritation, chemesthesis)\(^{121}\), originates in delocalised stimulation of trigeminal nerve endings\(^{281}\) — a sharp, stinging or partial sensation of flavour or odour\(^{4}\). Individuals are generally more sensitive to aroma notes than pungency\(^{233}\).

In maturations, pungency is generally replaced by smoothness\(^{85,206}\). Ethanolic-pungency, often ascribed to ethanol content, is not solely from spirit strength: activity of headspace ethyl esters also contributes\(^{281}\). The off-note peppery-pungency originates in bacterial, notably *Lactobacillus*\(^{105,136,140,241}\) spp., fermentations producing acrolein\(^{105,160}\) at elevated temperatures or in extended fermentations\(^{241}\), from glycerol from yeast catabolism. The product, \( \beta \)-hydroxy propionaldehyde, is in distillation\(^{38}\) degraded to lachrymatory acrolein — inducing pungent, burnt and peppery notes\(^{90}\), red eyes\(^{160}\). Wooden washbacks
Fig. 4. Lignin-derived aromatic aldehyde transformations in whisky.
are sources of bacterial contamination but pH, oxygen tension, agitation, presence of yeast cells and/or mash residue, fermentable sugars and glycerol influence acrolein production\textsuperscript{160}. After 2–3 maturation years, these off-flavours disappear: acrolein reacts with ethanol yielding 1,1-diethoxy-2-propene\textsuperscript{38,138} and propene\textsuperscript{105,106,177}. None possesses unpleasant notes or lachrymatory effects. Peppery attributes should be discriminated from spicy-peppery character from certain casks.

### Phenolic characters

**A. Peaty character**

A.1. burnt – tarry, sooty, ash
A.2. smoky – wood smoke, kippery, smocked bacon/cheese
A.3. medicinal – TCP, antiseptic, germoline, hospital

Smoky is linked to degraded wood carbohydrates – cellulose, hemicelluloses and lignins\textsuperscript{37}. Peaty attributes originate in smoke, introduced into the airflow during the kilning processes\textsuperscript{11,12}, from phenolic compounds\textsuperscript{280} and also sulphur- and nitrogen congeners, pyridines and thiazoles. Quantitatively important are phenol, cresols \(\text{m-}, \text{o-}, \text{p-}\), xyleneols, and \(\text{p-}\) and \(\text{m-}\) ethylphenol. Guaiacol has low flavour thresholds (3 \(\mu\)g litre\(^{-1}\) in 10\% spirit\textsuperscript{66}; detection, 0.09 \(\mu\)g litre\(^{-1}\) and recognition 3 \(\mu\)g litre\(^{-1}\) \textsuperscript{127}) and substituted methoxy phenols\textsuperscript{278} have significant flavour impacts. Important volatiles for desirable smoke flavour are abundant in phenolic and basic subfractions, acidic and neutral are of secondary importance\textsuperscript{37}.

Although kilning uses alternative fuels, inclusion of short-time intensive peat combustion yields a characteristic \textit{reek}. Smoke absorption is maximal at 15–30\% moisture in malting barley\textsuperscript{11}. Raising kilning from 400 to 750\°C yields several-fold increases in phenol and cresol, reducing guaiacol\textsuperscript{11}. Thomson\textsuperscript{257} has reviewed relationships between flavour-active phenols, peat and stillage attributes following extraction of thermally degraded lignins (Fig. 4) with ethanolysis of Braun’s lignin\textsuperscript{126}. The resulting aromatic aldehydes induce \textit{sweetness} and \textit{smoky} attributes\textsuperscript{43,44}. Other phenolics – e.g. benzoic, cinnamic, ferulic (4-hydroxy-3-methoxycinnamic)\textsuperscript{99}, \textit{p-coumaric} (4-hydroxycinnamic) and sinapic acids – originated in cereal cell walls (Fig. 5) and are transformed into phenols by kilning, thermal decarboxylations\textsuperscript{261}. Ferulic and \textit{p-coumaric} acids yield 4-vinyl guaiacol and 4-ethyl phenols, respectively (Fig. 4), through yeast decarboxylations\textsuperscript{36,59,60,243} particularly in spirits from rye abundant in phenolic acids\textsuperscript{109}.

Hydrophilicity in phenols ensures feint retention limiting final whisky concentration\textsuperscript{58,189}. Phenol dominates (46–67\%) in peated barley malt, cresols (58–61\%) final spirit. Both, from peated malts, influence character of Scotch, Spanish and Japanese whiskies\textsuperscript{67}. O-cresol is most abundant in Scotch whisky with thresholds of 31 \(\mu\)g litre\(^{-1}\) in 10\% spirit\textsuperscript{66} and 30 and 120 \(\mu\)g litre\(^{-1}\) (detection and recognition) in 23\% grain whisky\textsuperscript{127}. Phenol contributes only circa 7\% odour units\textsuperscript{16,225} but related attributes are important, especially in Scotch whisky\textsuperscript{280} with characters often described as \textit{medicinal} and \textit{iodine}\textsuperscript{23}. In Speyside malts this is more often \textit{peaty}. Strong phenolic characters such as \textit{medicinal} relate to kilning \textit{o-} and \textit{m-cresols}, \textit{peaty} may be linked to eugenol\textsuperscript{250}. In Bourbon and Canadian whiskies unpeated, green malts from barley, corn or rye, and phenol and cresols have lesser impacts on character and \textit{smoky} attributes originate in lignin breakdown components. These included eugenol, 4-ethyl phenol and 4-ethyl guaiacol, from new staves after charring and ethanolic extractions\textsuperscript{131} (Fig. 4) or cereal cell walls. Eugenol with low thresholds of 11\%, and detection at 0.5 and recognition of 5 \(\mu\)g litre\(^{-1}\) \textsuperscript{127}, influences Bourbon flavour\textsuperscript{66}. Adding phenol mixtures to Bourbon mimicked Scotch whisky characters of \textit{woody} with additional oily, but not \textit{esters} and \textit{sweet} attributes\textsuperscript{66}.

Humic and fulvic acids in mashing waters\textsuperscript{172,272} influence \textit{peaty} characters. Congeners including halogens of marine origins\textsuperscript{172} and microbial activity also generates highly flavour-active compounds such as chloroguaiacols that at extreme dilutions yield distinctive off-notes, e.g. \textit{Rio} character in coffee\textsuperscript{55,146,240}.

In the original flavour wheel\textsuperscript{233}, discrimination of phenolic attributes was contentious with secondary tier clustering of \textit{medicinal}, \textit{peaty} and \textit{kippery}. Relationships between the stronger \textit{medicinal}, and \textit{peaty} are unclear\textsuperscript{12,250} as are those between \textit{peaty} and \textit{dry} attributes in whiskies\textsuperscript{171}. No relationship between \textit{dryness} of Scotch and total phenol content has been demonstrated\textsuperscript{12,251}. Interestingly, a specific volatile phenol anosmia – partial odour blindness – is reported in 15\% of the UK population for suggesting inconsistent flavour influences\textsuperscript{8}.

### Fermentation characters

**B. Grainy characters**

B.1. cereal – (digestive) biscuity, husky, bran, leathery, tobacco, mousy
B.2. malt – malt extract, malted barley
B.3. mash – porridge, draff, wort, cooked maize

Grainy characters, unlinked to any specific congener, are regarded by distillers as important. Raw materials, grains or cooked grain (mash) form reference standard. Green malts confer \textit{fruity}, \textit{hay-like}, and \textit{damp straw} notes, replaced by \textit{burnt}, \textit{bready}, \textit{malty} and \textit{chocolate-like} notes\textsuperscript{14} with increased kilning temperatures. Maillard browning intermediates interact with cereal lipid oxidation products (Fig. 5).
Furfural, *grainy* at 20–30 mg/litre in Scotch whisky\(^{138}\), may contribute to *hotness* in spirits\(^{86,238}\). At 90% recognition threshold (839 mg/litre)\(^{129}\) furfural was described by few distillers (<10%) as *grainy*, more used was *marzipan* (coconut, cake mix, almond, nutty, walnut oil and *coumarin*-like – 54%), *sweet* (26%) and *oily* (15%)\(^{129}\). Pentose sugars, from breakdown of cereal cell walls, yield furfural during pyrolysis in malting and distillation\(^{1217-176-338}\) (Fig. 5): concentrations are functions of wash pH especially with high numbers of lactic bacteria\(^{17}\).

In whole and ground cereals\(^{229}\), aldehydes, enals, 2,3-butandiol, acetic acid, and chloro- and bromomethoxybenzenes dominate volatiles. The last is associated with *malty* in sorghums. In malts\(^{13}\) *malty* is associated with 2- and 3-methylbutanal, linked to *warty* in alcohol-free beer\(^{193,194}\). Perpète and Collin\(^{193,194}\) associated *warty* primarily with 3-methylthiopropanaldehyde but other compounds influencing *malty* or cereal-like character include ethylmethylpyrazines, maltol\(^{13}\) and hydroxymethylfuranone from 2-methylpropanal\(^{71}\). Fermented malt extracts typically contain 4-hydroxy-5(or 2)-ethyl-2(or 5)-methyl-3(2H)-furanone (HEMF) and 4-hydroxy-2,5-dimethyl-3(2H)-furanone (HDMF). All produced in beer by *Saccharomyces cerevisiae*\(^{44}\) have sweet, *malty* and *caramel* notes.

### Aldehydic characters

#### C. *Grassy* character

C.1. *fresh* – *leafy, wet/cut grass, flower stem, green apple, banana*

**C.2. dried** – *hay, straw, tea, mint, herbal*

*Grassy* is often synonymous with *aldehydic*, *green* and *leafy* attributes\(^{233}\) but the technical – *aldehydic* – is better understood as *fresh* and *dried grassy*\(^{129}\). *Grassy* is better defined than *green*, widely used for immaturity in wines (young), from green malt usage\(^{233}\) and multifaceted in perfumery\(^{102}\). *Grassy* notes from hexanal are perceived *almond* by a minority (12%) of assessors\(^{129}\).

Many compounds relate to *grassy* characters in whisky\(^{26,106,246,247,251,278}\) including low molecular weight aldehydes e.g. hexanal, trans-2-hexenal, 2- and 3-hexenol. These confer *green leaves*, *grassy* and even *fruity* notes. Increasing aliphatic chain length yields less pleasant *cardboard*-like and *bitter* notes\(^{156}\). Aldehydes originate in barley lipids, dominated by 9,12-octadecadienoic (linoleic), 9,12,15-octadecatrienoic (linolenic) and 9-octadecenoic (oleic) acids. Malt lipooxygenases oxidise linolenic and 6,10,14,18-eicosatetraenoic (arachidonic) acids (Fig. 5), yielding 9- and 13-hydroperoxides and further aldehydes: hexanal, trans-2-hexenal\(^{189}\), 2- and 3-hexenol (leaf alcohol)\(^{54,102}\) and unsaturated methyl ketones (6-tridecen-2-one, 6-pentadecen-2-one and 6-heptadecen-2-one)\(^{275}\).

### Estery characters

Estery characters are ordered as in the original wheel\(^{233}\), and include *solvent*, *fruity*, *floral*, and *feinty*, functions of aliphatic chain length\(^{219}\). In distillations, *solvent* and *fruity*, are related to heads (foreshot), passing to *floral* and *feints* (tails) as distillation proceeds\(^{96,189}\)
(Fig. 6). Spirit cut-off points are central to estery characters and differ between distilleries. Although individual esters showed less impacts on whisky flavour, in total, esters form a key component of flavour, contributing particularly to complex roundness.

In fermentations, acetyl CoA reacts with free alcohols to form esters at rates which are inversely related to aliphatic chain length, and yields determined by fatty acids concentrations (Fig. 5). Effective concentrations vary: ethyl caproate (C6) is released into wash, laurate (C12) largely retained within yeast cells. Fermentation ester formation is influenced by wort gravity, yeast strain and pitching rate, wort unsaturated fatty acid concentration, aeration and temperature. Mass transfer of substrates, and yeast growth, are key factors for wort levels of medium-chain fatty acids.

In maturation, further esterification of fatty acids occurs, and ethyl acetate becomes abundant originating in acetic acid from hydrolysis of hemicellulose acetyl groups, oxidation of ethanol, and wood charring. Equilibria exist between acetaldehyde and ethyl acetate; between ester and acetic acid and ethanol. Certain acids, notably hexanoic (caproic, C6) and tetradecanoic (myristic, C14), react slowly in maturations and others - ethyl decanoate (caprate, C10), hexadecanoate (palmitic, C16) and 9,12,15-octadecatrienoate (linoleate: C18) - show significant reverse reactions.

The first-light fraction (foreshots)

D. Fruity characters
D.1. solvency - nail vanish remover, paint thinner, fusel oil
D.2. orchard - apple, peaches, pear
D.3. tropical - pineapple, melon, banana (pear-drop)
D.4. citrus - orange, lemon, grapefruit, zest
D.5. berries - blackcurrant, tomato plant, catty
D.6. dried - raisins, figs, prunes

Ester characters - e.g. from ethyl acetate the most abundant at (typically) 175 mg litre⁻¹ in whisky are often perceived solvent-like. Ethyl acetate has high thresholds of between 33 and 74 mg litre⁻¹ with detection and recognition thresholds in 23% (abv) grain spirit of 14 and 100 mg litre⁻¹, respectively. However, esters show synergistic and suppression effects that could influence overall character.

Short-chain alcohol esters (foreshots) (Fig. 6) - ethyl, iso-butyl and iso-amyl esters and iso-amyl alcohol are perceived as fruity, mainly banana or apple. These congeners influence quality in relation to spirit content of fusel oils; in whiskies ethyl acetate and related esters, impart pear-drop characters.

Dried-fruity notes in dried bell peppers are linked with 2-methylpropanal, and 2- and 3-methylbutanal, also linked to malty and worty notes in malts.

The middle fraction (spirit)

This fraction is abundant in ethyl hexanoate (caproate, C6), octanoate (caprylate, C8), decanoate (caprate, C10), dodecanoate (laurate, C12) and lactate, which are important in whisky flavour. Ethyl hexanoate (caproate, C6) imparts fruity (appley) characters and with increasing ester chain length soapy, oily and sour notes, related to whisky immaturity. Such notes, abundant in later stages of batch distillation, are associated with ethyl octanoate (caprylate, C8) and esters of tetradecanoic (myristic, C14), and hexadecanoic (palmitic, C16) and hexadecenoic (palmitoleic, C18) acids.

The tail fraction (feints)

Hexanoic (caproic, C6), octanoic (caprylic, C8), decanoic (capric, C10) and dodecanoic (lauric, C12) acids and esters of dodecanoic (lauric, C12), tetradecanoic (myristic, C14), hexadecanoic (palmitic, C16) and hexadecenoic (palmitoleic, C16:1) acids yield soapy, oily, sour and feints notes, often discarded as tails. Excess higher fatty acid esters (>C₁₄₆) cause chill haze in spirit reductions to bottling strength and are less desirable in new distillates. Feints notes, infrequent in early spirit fractions, are linked to certain fatty acids and sulphur congeners.

E. Floral characters
E.1. natural - rose, lavender, violet, bluebell, carnation, heather, honey
E.2. artificial - fragrant, scented, perfumed

In feints phenylethyl ethanol confers floral, rose-water and fragrant notes; β-damascenone, an impact compound in Damascus rose oil, imparts fragrant with dilution to 2% (abv). This β-damascenone has a high odour unit value in whisky, but low intensity index limits detection. Autodissolved of vitamin A or lipids, from yeast or barley, and breakdown of oak nortisolrenoids yields α- and β-ionones with violet-like notes.

F. Feints characters
F.1. grainy: see section B
F.2. cheesy: see section K
F.3. oily: see section L
F.4. sulphury: see section J

Excess feints notes influence distillate quality. Notes include leathery or cereal-like (cooked mash, biscuity) passing...
to sweaty (piggery) and into stale fish characters\textsuperscript{233}. Sweaty is related to isovaleric acid content\textsuperscript{168}. Feints, with distinctive stale notes and metallic aftertaste\textsuperscript{11}, have abundant malt-derived phenols and DMTS\textsuperscript{27}.

**Maturation characters**

**G. Woody character**

White oak wood (\textit{e.g. Quercus alba}) varies in contents\textsuperscript{57} of cellulose (49–52\%), lignin (31–33\%), hemicellulose (22\%) and extractable compounds: volatile lipids, volatile and non-volatile acids, sugars, steroids, tannic substances, pigments and inorganic compounds\textsuperscript{172}. Heartwood contains more lipids: triglycerides of C\textsubscript{18} unsaturated and C\textsubscript{16} saturated fatty acids, sterols and a ferulic acid ester with a C\textsubscript{40} wax alcohol\textsuperscript{238}. All have \textit{gradual impacts} with cask ageing and staves producing hazes during spirit reduction for bottling\textsuperscript{238}.

Cellulose (a glucose homopolymer) is central to oakwood structure with hemicelluloses (heterogenous polymers) forming matrices and lignin an adhesive encrustant. Cell wall lignin (70\%) is linked to hemicelluloses in a three-dimensional complex dominated by phenylpropane derivatives of guaiacyl (2-methoxyphenol) and syringyl (2,6-dimethoxyphenol) units with aliphatic and aromatic intermonomer covalent bonds. Linkages between lignin, tannins and the carbohydrates make fractionation difficult and insolubility reduces flavour impact. However, breakdown products and related extracts influence flavour\textsuperscript{238} conferring smoky\textsuperscript{37} and woody characters. In charring, lignins are more stable than polysaccharides\textsuperscript{37}. In acidic (\textit{pH} 4.5) wood maturation\textsuperscript{172,37} insoluble hemicelluloses slowly depolymerise and are extracted.

Woody characters are complex in both whisky and wines\textsuperscript{178}. Important contributors include lipid-derived whisky lactones, and lignin breakdown compounds – vanillin, and related aromatic aldehydes, and derived acids, esters, tannins and sugars. Pérez-Coello and coworkers\textsuperscript{192} regarded \textit{cis}- and \textit{trans}-lactones, eugenol, vanillin and syringaldehyde as the volatiles with greatest sensory impact with optima for extractions of vanillin and syringaldehyde at 165–215 °C\textsuperscript{131}. A syringaldehyde/vanillin ratio of 1.4/2.5 indicates vanillin and syringaldehyde of 165–215 °C\textsuperscript{151}. A greatest sensory impact with optima for extractions of vanillin, and related aromatic aldehydes, and derived whisky lactones, and lignin breakdown compounds - wines\textsuperscript{178}. Important contributors include lipid-derived components and associated notes\textsuperscript{238}.

Higher alcoholic strength fillings reduce extraction of wood-derived components and associated notes\textsuperscript{238}. In an 8-year old whisky, filled at 59\% abv, character was flavoured, at 63\% less matured and weaker and at 77\% green oak\textsuperscript{172,238}. In cognac, extractions of phenolic acids, aromatic aldehydes, acetals, ethyl butyrate, medium chain fatty acid esters (C8, 10 & 12), were maximal at 60–70\% abv; sugars, polyols, ethyl acetate, and acetic and short chain fatty acids (C3, 4 & 5) at 40–50\% abv\textsuperscript{24}. For balanced extractions the optimum was 50–55\% abv\textsuperscript{24}, typical of armagnac.

**Wood extractive characters**

G.5. nutty – coconut, hazel nut, almond/marzipan, walnut

\textit{Nutty} is associated with a product of oak lipid oxidation, described as “whisky lactone”, “3-methyl-4-octanolides”, “β-methyl-γ-octalactone”, “5-butyl-4-methyl-dihydro-2(3H)-furanone”, or “Quercus lactone”. Associated flavour character is coconut at high concentrations (>5.3 mg litre\textsuperscript{-1}) and oak \textit{wood-like} at lower (0.1 mg litre\textsuperscript{-1})\textsuperscript{139,231}. This lactone, together with 4-nonanone and eugenol\textsuperscript{140,154}, are major volatile congeners derived solely from oak\textsuperscript{142,238}. A possible lactone precursor is 2-methyl-3-(3,4-dihydroxy-5-methoxybenzoyl)-octanolic acid\textsuperscript{152,183}.

Four lactone isomers are, \textit{cis}- (3R,4R), \textit{cis}- (3S,4S), \textit{trans}- (3S,4R) and \textit{trans}- (3R,4S), differing in flavour character (Table II)\textsuperscript{83}. Oak contains only \textit{cis}- (3S,4S) and \textit{trans}- (3S,4R)\textsuperscript{152,155}; other isomers indicate synthetic lactones in flavouring/ageing agents\textsuperscript{143,164}. Misidentification of isomers\textsuperscript{21,110,142,139,184} has produced contradictory \textit{cis}:\textit{trans} ratios, and threshold values\textsuperscript{33,142,163,184}. 

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### TABLE II. Taste and odour properties of oak lactones.

<table>
<thead>
<tr>
<th>Compound</th>
<th>Taste</th>
<th>Odour</th>
</tr>
</thead>
<tbody>
<tr>
<td>cis-(3R,4R)</td>
<td>Creamy, coconut</td>
<td>Sweet, woody, coconut</td>
</tr>
<tr>
<td>cis-(3S,4S)</td>
<td>Spicy, coconut-like</td>
<td>Light coconut, musty, hay</td>
</tr>
<tr>
<td>trans-(3S,4R)</td>
<td>Coconut-like, sweet, creamy, farty</td>
<td>Spicy, celery, slight coconut, green walnut</td>
</tr>
<tr>
<td>trans-(3R,4S)</td>
<td>Spicy</td>
<td>Coconut, celery</td>
</tr>
</tbody>
</table>

( Günther et al., 1986; reproduced with permission from *Leibigs Annalen der Chemie*, 1986, 2112)

For racemic mixture of lactones, detection and recognition thresholds were: 0.5 and 1 mg litre\(^{-1}\), respectively in 23% grain whisky but 0.05 mg litre\(^{-1}\) in 34% abv grain spirit; in white and red wines 120 and 125 µg litre\(^{-1}\) respectively in 23% grain whisky but 0.05 mg litre\(^{-1}\) in 34% abv grain spirit; in white and red wine lactone confers musty notes, in red harsh and in 12% ethanol coconut, woody and oaky linked to the more abundant cis isomer (Table II) with a threshold of 0.092 mg litre\(^{-1}\), 2.5-20 times lower than trans. Wood origins can be related to lactone ratio\(^{192}\), reported\(^{77,23}\) (cis:trans) in wood but dependent on cask history and treatment. The cis lactone is more abundant in American white oaks than Pedunculate or Sessile\(^{152}\). Ratios (cis:trans) also vary through single staves, with cis maximal (250 mg kg\(^{-1}\) of wood), and more extractable\(^{143}\), at 5 mm below stave surface and trans maximal (48 mg kg\(^{-1}\)) at 15 mm depth\(^{44}\).

Lactones have been studied extensively as important in wine characters\(^{1-2,14}\). Waterhouse and coworkers\(^{271}\) have controversially claimed ratios in wine maturation oaks (European versus American oak) suggest white oaks showed fixed ratios of cis to trans oak lactone, determined genetically\(^{143}\). American white oak (Quercus alba) heartwood contains five-fold more lactone and precursor lipids\(^{142}\) than sapwood: two 3-oxo-retro-α-ionol isomers serve as markers. However, eugenol and vanillin concentrations are similar in American and European oaks\(^{31}\). European pedunculate oak (Quercus robur), low in aromatics and high in ellagitannin, is best suited to ageing spirits; European sessile (Quercus petraea) and American white oak to maturing wine\(^{31}\). New Bourbon casks have ten-fold higher extractable lactones than Scotch casks at 0.047-0.254 µg kg\(^{-1}\): flavour impact is reduced by cask usage\(^{44}\). “Standard” Scotch whisky have been reported containing 0.96, “premium” 1.16, and a “high” had 2.17 mg litre\(^{-1}\) total lactone\(^{184}\). Similar correlations between lactone concentrations and quality grade exist in cognacs\(^{184}\). There is conversion of trans to more stable, flavour-active cis form in bottle maturation of wine\(^{35}\).

Thermal lipid oxidations\(^{142}\) in cask charring increases lactone up to three-fold but excess temperatures reduce surface content\(^{33,142}\). Lactone is retained deeper in staves, and below chars. Care during charring is beneficial as changes in cis/trans ratio will influence character\(^{143}\). In wines (e.g. Chardonnay), green oak yields vanilla, buttery, nutty, caramel, coconut, raisin and dill notes, and increases spicy characters\(^{237}\). In contrast, seasoned wood increases cedar and nutty notes, decreasing raisin\(^{24,227}\).

Other lactones, γ-nonalactone (C9L), γ-decalactone (C10L) and γ-dodecalactone (C12L) are found in mature and immature malt whiskies, imparting fatty, and sweet notes – particularly C10L and C12L in malt whisky\(^{264}\). Certain yeasts, notably Sporobolomyces, in specific wines and flor sheries, excrete 4-decanolide and cis-6-dodecen-4-olide\(^{18,567}\).

G.6. vanilla – ice cream, custard, toffee, chocolate, cake mix, cola

Vanilla, often described chocolate and cola through “circle minded” associations\(^{102}\), is important in certain whiskies. New casks are toasted to eliminate new-wood notes and astringent tastes, with an optimum of 165–215°C\(^{151}\) for Bourbons. Charring increases contents of vanillin, vanillic acid and related compounds – acetovanillone and propiovanillone, and other lignin aldehydes – coniferaldehyde, sinapaldehyde, acetosyringone – and their acids\(^{177}\). Aldehydes are oxidised to acids or converted to vanillin and syringaldehyde contributing to vanilla (Fig. 4)\(^{176,177}\) with effects\(^{10,50,176,217}\) including synergistic interactions (Table III)\(^{179}\). Clyne\(^{40}\) linked increased vanillin and syringaldehyde in whisky from charred casks with smooth, vanilla, sweet, nutty, spicy, fruity and floral notes reminiscent of Bourbon whiskey. Whisky matured in uncharred casks had higher contents of coniferaldehyde, sinapaldehyde and vanillic acid with pungent, grainy, sour, oily, sulphury, catty, nutty, and fishy notes. Gallic acid from tannin hydrolysis is most abundant in uncharred woods, in Scotch whisky the flavour impact...
of syringaldehyde (50% of total aldehydes) and vanillin (24%) is thought greater. Increased dissolved oxygen yields higher concentrations of vanillin, syringaldehyde, coniferaldehyde, vanillic and syringic acids. Extraction rate is high immediately after filling and slower during subsequent maturation promoted by hydrolysis, ethanolysis and also oxidations, at rates determined by filling strength. 

Thresholds for vanillin have been defined as 2 mg litre$^{-1}$ in water, 0.5 and 0.1 mg litre$^{-1}$ in 10 and 40% ethanol solutions. These sensorially-important phenols are maximal at 5 mm below the char in new wood with syringaldehyde and syringic acid more abundant than vanillin and vanillic acid. Oak wood drying (air or kiln) also influences vanillin, coniferaldehyde and syringaldehyde contents. Air seasoning may increase mycoflora attacking cell wall lignins and polysaccharides, yielding compounds associated with positive maturation characters.

G.7. spicy – clove, cinnamon, ginger, 'aromatic', nutmeg

Woodsy spicy attributes originate in wood extracts, particularly eugenol, derived from lipid oxidation (Fig. 5), abundant in Bourbon whisky. This congener has a thresholds 2-34 µg litre$^{-1}$ in beers in 10 and 20% ethanol respectively and detection and recognition thresholds of 0.5 and 4.9 mg litre$^{-1}$ respectively in 23% abv grain spirit. Lignin thermal degradation products such as vinyl-, allyl- and ethyl guaiacols, guaiacol (2-methoxyphenol), cinnamaldehyde and related phenolic acids contribute sweet, smoky and spicy notes (Fig. 4). The yeast enzyme ferulic acid decarboxylase converts cell wall ferulic acid to 4-vinyl guaiacol. The related clove has a character linked to oakiness. However spicy notes are common to clove, cinnamon bark oils, and other spices and distinctions may be difficult necessitating specialised sensory training.

G.8. caramel – candy floss, treacle, coffee, toast, liquorice

Caramel – sweet, burnt and notably smoky notes originate in thermal breakdown of lignins, dominated by phenols such as guaiacol (2-methoxyphenol), 4-acetyl-guaiacol and syringol (2,6-dimethoxyphenol), homologues and derivatives. The stability of lignin polymers limits their contributions to maturing spirit but lower molecular weight guaiacyl and syringyl products are extracted in concentrations decreasing with repeated use. Certain flavour notes originate in 5-hydroxymethyl-2-furfuraldehyde and hydroxymethylpyranones from ageing in freshly charred casks. Caramel added to enhance colour in blended whiskies also contains 5-hydroxymethyl-2-furfuraldehyde. In Bourbon whiskey, 2-hydroxy-3-methyl-2-cyclopentenone and 3-hydroxy-2-methyl-4-pyrrone (maltol), with sweet and burnt notes, are important.
Other stave pyrolysis-derived congeners, from Maillard reactions (Fig. 5), are furans: furfural, 2-methyl furfural and 5-hydroxyfurfural, and heterocyclic nitrogen compounds including pyrazines, pyridines, thiazoles, aliphatic amines, quinolines and pyrans40,41,142,177,210. Abundant nitrogen compounds, e.g. methylpyrazine and 4-methyl-5-vinylthiazole, impart burnt, roasted and nutty notes to malts and also contribute to flavour in whiskies. Such compounds are more abundant in char layers than in plain wood shavings or deeper layers210. Concentrations in whiskies are significantly higher than odour thresholds185. Pyrazines are regarded as having pleasant flavour notes: burnt, toasted, medicinal, nutty, fruity, woody and earthy210,263, but also phenolic, nutty and green. Flavour notes are enhanced when methoxyl groups are present on pyrazine derivatives145. Unlike pyrazines, pyridines are perceived as less pleasant: astringent, bitter, buttery, caramel, roasted, green, earthy, rubbery, and fatty144, and pungent, solvent and fishy60. Viro266 showed reducing pyridines in Finnish whiskies improved flavour. Such pyridines are ionized at low pH (4.0-4.5) in matured whisky, and therefore flavour impacts are low56,210.

G.9. Previous use - sherry, Bourbon, port, rum, brandy, wine

Scotch whisky has traditionally been matured in reused sherry, Madeira and port casks that flavour spirit. Shortage of ex-sherry, replaced by ex-Bourbon, barrels31,164 has promoted pressure pre-treatments with white wine or sweet, dark sherry that increase final ester and sugar contents yielding mildly flavoured whiskies164.

Other wood extractive characters

Mellowness, roundness & smoothness

Mellowness and lingering aftertastes are related to changes in hydrogen bonding in spirit during maturation, with formation of ethanol cluster structures23,177. Such clusters can be deduced from differential scanning calorimetry (Fig. 7)112 and adiabatic expansion studies under vacuum79,174 of immature and mature whiskies. Non-volatile oakwood extracts (Fig. 7)114,177 stabilise clusters, increasing mellowness and roundness with accumulation40,205,266. Such non-volatiles are monosaccharides (pentoses and hexoses) and aromatics from cell cask walls and glycerol216 from thermal breakdown of wood triglycerides.

Defective wood characters

G.10. mothball – paraffin, naphtha, camphor
G.11. musty – mouldy, earthy, fusty, corked
G.12. vinegary – acetic, sour

Mouldy and earthy notes appear to originate in fungi and actinomycetes on malts272, defective casks198 and cork closures, notably Armillaria mellea222,228,236,237 on corks. In wines such aroma notes are linked to methyl thiopyrazine, 2-acetyl piperidine and its isomer 2-acetyl tetrahydro pyridine, 1-octen-3-one (mushroom), 3-octen-1-one (musty, mouldy, earthy, mushroom)32. Musty, or cork taint notes are associated with 2-methyl-isoborneol (2-MIB (earthy), geosmin (mildew) and 2,4,6-trichloroanisole (2,4,6-TCA)69,237. Other contributors include 2,3-diethyl-5-methylpyrazine and 2-isopropyl-3-methoxypyrazine (musty/mouldy)101,124. Corks contaminated with moulds and pesticide chlorophenols 6-chlorovanillin, 4-chloroguaiacol, 4,5-dichloroguaiacol and veratrole yield chloroanisoles (e.g. 2,4,6-TCA) with corked taint and musty. These are important in tainted wines28,29,77,118 and other drinks63, originating in woods, including shavings124. In wine, the low thresholds248 show a bimodal distribution, at 1.461 and 17.4-210 ng litre-1. Certain individuals are particularly sensitive to such flavour notes236. Before surface treatments, corks yield woody and green cork notes and after less woody and more oily from coating materials236. Off notes of microbial origin are reduced by autoclaving222.
Geosmin, and 2-MIB, with low detection thresholds (ng litre\(^{-1}\), introduced in water\(^{156,200}\), are unstable in the acidic environments of wines and spirits.

H. **Sweet characters**

H.1. *woody-sweet*: see section G
H.2. *floral-sweet*: see section E
H.3. *fruity-sweet*: see section D
H.4. *buttery-sweet*: see section L

Sweet characters are important in whisky flavour but their origins are not clear. In 23% abv grain whisky, sweetness can be evoked by diacetyl (47% respondents), maltol (38%), vanillin (28%), furfural (26%), ethyl hexanoate (24%), iso-amyl acetate (15%), whisky lactone (10%)\(^{129}\). Certain assessors used only the generic description *sweet* and did not specify between them which reflects either lack of verbal ability or physical properties of congeners. Vanillin is linked to *woody-sweet*, also vanilla (58%), toffee (35% – toffee, caramel, fudge and chocolate) and sweet (28%). Whisky lactone was described as coconut (84% of respondents), but has also a sweet almond character (*nutty*, 11%, marzipan, 7% and almond, 4%)\(^{129}\). *Nutty* is related to sweet taste character\(^{102}\). 4-Vinyl guaiacol contributes *sweet-woody* character to whiskies. *Sweet-smoky* (32%) is linked to wood-derived phenols: spicy (17% – spicy, nutmeg, ginger, clove and aromatic), vanilla (13%) and woody (7%). Maltol evoked candy floss in 44% respondents, with frequent usage of related terms – *sweet* (39% – sweet and sugary) and caramel (35% – caramel, burnt sugar, toffee).

As for *floral-sweet*, geraniol was described as *floral* (36%), lemony (citrus and washing-up liquid, 25%), scented soap (21%), but also sweet (17%)\(^{129}\). As for *fruity-sweet*, isoamyl acetate was described as *sweet-corn* (67%). Other *fruity-sweet* terms in 23% abv grain whisky, were banana and pear (22%)\(^{129}\) and *buttery-sweet*: discrimination of perceptions of *sweet* and *buttery* are difficult with diacetyl at 90% recognition threshold\(^{129}\). Diacetyl was sweet to 47% respondents and *buttery* to only 31%\(^{129}\).

I. **Stale characters**

I.1. *cardboard* – papery, filter sheet
I.2. *metallic* – inky, tinny, wet iron, rusty: see the section F (feints)

Cardboard-like notes generally originate in lipid oxidations of unsaturated fatty acids from cereals or yeast metabolism\(^{18,82}\).

Lipoxygenase oxidation of 9,12-octadecadienoic (linoleic) and 9,12,15-octadecatrienoic (linolenic) acids yields pentanal, hexanal, nonanal, (E)-octenal, 2,4-heptadienal, (E)-2-nonenal, (E,E)-2,4-nonenal and 2,4-decadienal responsible for *cardboard* in boiled potato\(^{106}\). Hexadecenoic (palmitoleic) acid autoxidation yields (E)- and (Z)-2-nonenal and (E)-2-octanal with *cardboard* notes in butter \(^{227}\). (E)-2-nonenal in 23% abv grain whisky was described as *cardboard* with detection and recognition thresholds of 3 and 8 µg litre\(^{-1}\), respectively\(^{130}\).

J. **Sulphury characters**

J.1. *stagnant* – sewer, drains, foul water, rotten vegetable
J.2. *meaty* – yeasty, Marmite, rotten egg
J.3. *vegetable* – turnip, potato, cooked vegetable (sweetcorn, boiled cabbage)
J.4. *sour* – pickled onion, garlic
J.5. *gassy* – town gas, burnt match, acid
J.6. *rubbery* – tyre/tubes, pencil eraser, plastic

Sulphur compounds are important sources of off-flavours reducing spirit quality\(^{27,133,153}\), although low concentrations in beers enhance acceptability\(^{18}\). Water dilutions enhanced flavour impact through hydrophobicity, although such volatility is suppressed by wood-derived congeners\(^{207}\). In lagers, dimethyl (DMS) and diethyl sulphide have low thresholds at 30–50 and 0.4 µg litre\(^{-1}\), respectively, and thiols at <2 µg litre\(^{-1}\)\(^{-1}\). In beer DMS above 100 µg litre\(^{-1}\) imparts cooked sweet-corn, spicy and *malty*\(^{128}\) or blackcurrant-like\(^{7}\) notes; at lower concentrations flavour impacts are not significant\(^{7}\). In lagers, ethanethiol evokes stronger gunpowder and acrid notes\(^{128}\). In 23% grain whisky detection and recognition thresholds of dimethyl trisulphide (DMTS) were 4 and 20 µg litre\(^{-1}\), respectively\(^{130}\), and 3–6 µg litre\(^{-1}\)\(^{-1}\). In beer associated flavour notes are *garlic* (onion, cabbage), *drains* and (struck) *match*\(^{128}\) and thresholds for H\(_2\)S are 6 µg litre\(^{-1}\)\(^{-1}\). In grain whisky perceptions were *rubbery* (21% respondent), *sour* (21%) and *gassy* (15%)\(^{129}\). Low molecular weight sulphur congeners confer light and neutral\(^{133}\) characters, medium as lightly bitter and roasted tinge and higher as heavy. *Meaty*, *burnt* and *thiamine-like* attributes are associated with methyl-(2-methyl-3-furyl)-disulphides (MMFD), bis(2-methyl-3-furyl)-disulphides, and methyl (2-methyl-3-furyl)-sulphides and 2,5-dimethyl-3-methylidithiofuran. The important congener MMFD, present in grain and malt whiskies, has low thresholds of 0.005 µg litre\(^{-1}\) in rectified and 0.10 µg litre\(^{-1}\) in grain spirit\(^{27}\). Other compounds derived from thiamine and amino acids also have low thresholds, <1 µg litre\(^{-1}\), and are important in roasted coffee\(^{266}\) and yeast extracts\(^{5}\).

Barley amino amino acids (cysteine, methionine) yield sulphur compounds (e.g. DMDS and DMTS) but in the absence of cysteine, DMDS, DMTS and methional are still formed during distillation\(^{79}\) possibly from thermally degradation of yeast metabolic products such as S-methyl-methionine through Strecker degradation to methional (Fig. 5) and methanethiol\(^{78}\). Dimethyl disulphide (DMDS) and trisulphide (DMTS) in new spirit are linearly correlated with wash methional.
although DMTS concentration can be modulated in still operation\textsuperscript{76,211}. Malathion used for pest control on barley might influence sulphur congener concentrations, but was reported to have no influence on final spirit\textsuperscript{256}.

Addition of rock sulphur or gaseous sulphur dioxide (SO\textsubscript{2}) during malt kilning reduces nitratosdimethylamine (NDMA) level through reactions between barley amines (especially hordeins in the rootlet) and fuel NO\textsubscript{2}. Most nitrosamines are unstable, evaporating before the kilning ‘break point’. Formation of NDMA is reduced by prior rootlet removal but influenced by hordein content\textsuperscript{290}. Sulphur dioxide at 10–30 mg litre\textsuperscript{-1} also reduces malt microbial loads\textsuperscript{211,228} and lightens colour. Wort pH is influenced by concentrations of SO\textsubscript{2} and sulphuric acid with effects on polysaccharide, glyco-proteins and glycolipid hydrolysis and wort concentrations of protein, α-amino nitrogen, lipids and fatty acids\textsuperscript{234}.

Malt yields DMS from S-methyl-methionine (SMM), absent from barley grain but increasing during germination\textsuperscript{224}. Temperature and moisture levels in barley at kilning influence conversion of SMM to DMS, with a boiling point of 38°C. Although evaporating during kilning and mashing, DMS is oxidised to dimethyl sulphoxide (DMSO) and dimethyl sulphur dioxide (DMSO\textsubscript{2})\textsuperscript{276,278}. Other sulphur congeners formed in mashing include carbonyl and hydrogen sulphides, methanethiol, carbon disulphide, sulphur dioxide and sulphoxide (DMSO)\textsuperscript{108}. Other sulphur congeners  

In fermentation, DMSO is reduced to DMS by sulphhydryl compounds during the fermentation. Anaerobic bacteria (Enterobacteriaceae) in certain washes also produce DMS from DMSO\textsuperscript{282}. Yeast autolysis yields DMDS, DMTS and certain other sulphur congeners\textsuperscript{11,211,244} at concentrations related to duration and intensity of wort heating. Yeast malic and citric acids\textsuperscript{18,211} promote hydrogen sulphide and sulphur-containing compounds secretion by lactic acid bacteria (Lactobacillus brevis, and L. fermentum)\textsuperscript{138}. Yeast metabolism also has a role, with storage at 5°C yielding less sulphur congeners than 20°C\textsuperscript{12}. Whisky mashes are susceptible to yeast infections, producing sulphides and further metabolic products (e.g. ethanethiol) through hydrogen sulphide reactions with ethanol\textsuperscript{18}. Strecker degradations (Fig. 5) of cysteine with diketone yield hydrogen sulphide (H2S) during fermentation, converted to ethanethiol and diethyl disulphide during distillation\textsuperscript{244}. Such H2S (typically at 9 mg litre\textsuperscript{-1}) interacts with residual maltotriose (0.8–1.4 mM) during distillation, yielding DMDS from methionine independent of the presence of copper ions\textsuperscript{79}. Notes from H2S were rotten-egg at high concentrations (ca 140 μg litre\textsuperscript{-1})\textsuperscript{128} and yeasty at 50 μg litre\textsuperscript{-1}\textsuperscript{258}. Supply of oxygen at distillation has little influence on sulphur compound formation as foam and carbon dioxide replace air in wash headspaces\textsuperscript{278}.

Copper interacts with sulphur compounds\textsuperscript{133} and reaction with copper ions is regarded as essential for producing clean spirit\textsuperscript{173,273}. Copper ions accumulate during wash distillation reaching 15 mg litre\textsuperscript{-1}\textsuperscript{78,213}. Cupric ions react with methional to produce DMDS, converted to other compounds as distillation progresses\textsuperscript{78}. As conversion is faster than formation\textsuperscript{78}, total DMDS concentrations in spirit are reduced.

Copper sulphate removes volatile sulphur congeners as non-volatile copper sulphides and mercaptides\textsuperscript{82}. Still deposits contain copper cyanides, thiocyanates, oxides and sulphates\textsuperscript{140}. This behaviour may be important for understanding spirit quality\textsuperscript{82}. Thiols react with surface copper oxide to form copper thiolates that in excess form complexes becoming self-assembled layers, with chemisorption\textsuperscript{109}. Thiolate layers react with congeners (e.g. thiophene) influencing sensory quality\textsuperscript{82}. However, chemisorbed thiol is limited (<4% of offered thiol concentration)\textsuperscript{109}. Distilling removes most sulphur compounds especially in predistillate (heads) and feint (tail) fractions: a copper still removed 70% dimethyl disulphide (DMDS) more than glass\textsuperscript{16,240} with similar findings reported for rum\textsuperscript{70}. For DMDS\textsuperscript{153}, however, glass distillation has been reported to show a ten-fold reduction over copper. Copper distillation also increases concentrations of other congeners: aldehydes, higher alcohols and esters but not carboxylic acids\textsuperscript{170}. The consensus is that copper distillation reduces sulphur congeners and positively influences sensory quality.

During maturation, oxidation of DMS to dimethylsulphoxide (DMSO) and dimethyl sulphur dioxide (DMSO\textsubscript{2}) continues: 50% of DMS was oxidized to DMSO and DMSO\textsubscript{2} after 96 h in a new cask\textsuperscript{76}. This was largely effected by the charcoal, and gallic acid was less effective. After 12 months, whisky DMS contents were low and a function of maturation parameters\textsuperscript{76} and DMTS contents decreased more slowly\textsuperscript{133,153}. Ratios of DMDS/DMTS form maturity indicators (30 for new-filling, 15 after 3 years\textsuperscript{133}. Either DMDS evaporates\textsuperscript{76} or is converted to DMTS until concentrations fall below flavour thresholds\textsuperscript{133}). Sulphur compounds – particularly, thiopehnes and polysulphides – can also differentiate products. Cask surface to volume ratios influence low molecular weight sulphur congener concentrations (DMS and DMDS) but not those of low-volatility aromatic sulphur compounds such as thiophene and thiazole\textsuperscript{153}. Addition of oak wood (chips) and air reduces sulphur congeners notably methionyl acetate and ethyl methionate\textsuperscript{276}.

K. Cheesy characters

K.1. rancid – ‘sickly sour’, baby vomit, oxidized fat
K.2. sweaty – old trainer/sock, musky, piggery

Bacterial action (Clostridia) yields n-butyric acid and ethyl butyrate\textsuperscript{26} with rancid (sickly) sour notes at low
mashing temperatures or if wash stands in cast iron vessels\textsuperscript{189}. Propionic, \textit{iso}-butyric and \textit{iso}-valeric acids have similar characters in whisky and are abundant in rum and brandy\textsuperscript{182}. In whisky \textit{iso}-valeric acid, present in concentrations related to yeast and fermentation conditions, dominates\textsuperscript{182}.

\textit{Rancio}, a Cognac character reminiscent of musty walnuts, can be confused with \textit{arnois} in whiskies. This \textit{rancio} character, indicating an old, well-stored cognac increasing with age in parallel with \textit{fineness} and \textit{mellowness}\textsuperscript{24}. The gradually acquired \textit{rancio} is from hydrolysis of fatty acid esters with oxidation to the ketones\textsuperscript{147}: 2-heptanone, 2-nonanone, 2-undecanone and 2-tridecanone. Concentrations are functions of peroxidases and cask volume\textsuperscript{264}. Long chain aldehydes, methyl ketones (C\textsubscript{7}, C\textsubscript{8} and C\textsubscript{11}), glyoxal and methyl glyoxal are related to \textit{rancio} characters in old wine-spirits (e.g. Armagnac, Cognac)\textsuperscript{19,264,265}. Glyoxal is present in whisky, but at concentrations too low to be quantified\textsuperscript{212} and \textit{Rancio} character has not been explicitly identified. \textit{Butter/ rancio} notes in wine\textsuperscript{2} are related to N-(3-methylthiopropyl) acetamide and 3-methylthiopropionic acid from methionol.

\textbf{L. Oily characters}

L.1. \textit{soapy} – waxy, unscented soap, detergent, damp laundry; see section F (feints)
L.2. \textit{buttery} – creamy, toffee, butterscotch
L.3. \textit{lubricant} – mineral oil
L.4. \textit{fat} – fatty, greasy, fish oil, castor oil

Buttery characters are related to diacetyl (2,3-butanedione), an off-note in lagers\textsuperscript{251}. Diacetyl and 3-hydroxy butanone are also important in wines, especially sweet Sherries\textsuperscript{150,279}. Diacetyl is produced by citrate-metabolising lactic acid bacteria\textsuperscript{8,253} and in yeast fermentations formed from \textit{a}-acetolactate and metabolised to acetoin. Yeast metabolism can be manipulated to produce acetoim directly from \textit{a}-acetolactate\textsuperscript{267}. In whisky nosing, diacetyl has a detection threshold of 0.02 mg litre\textsuperscript{-1}, a recognition of 0.04, and in tasting is 0.2 mg litre\textsuperscript{-1}\textsuperscript{257,267}. Fermentation oxygen influences spirit diacetyl content\textsuperscript{22}.

\textbf{T. Primary taste}

T.1. \textit{sweet}

Oak maturation influences time intensity factors (maximum intensity and duration) of sweet taste in sugar cane spirit (cachaca)\textsuperscript{25}. After 2 years there was little increase in peak intensity but a substantial increase in duration. Spirit changes can therefore influence perception of sweet character\textsuperscript{209}. In whisky, congeners conferring sweet are extracted from wood largely within 3 years\textsuperscript{216,226}. Glycerol primarily from wood triglycerides\textsuperscript{216} may also be generated by trans-esterification of triglycerides and ethanol, yielding fatty acid ethyl esters and free glycerol\textsuperscript{218}. In Bourbon whiskies stave hemicelluloses and acid-catalysed hydrolysis of tannins yield monosaccharides (arabinose, glucose, xylose, galactose and rhamnose)\textsuperscript{226}. Concentrations of most sugars increase in the early stages of wood maturation, but fructose and glycerol are still formed late in maturation (Fig. 8). Glucose, fructose, proteo-quinol and arabinose are reported the most abundant in whiskies\textsuperscript{30,165,181} with similarities in saccharide compositions in 12-month Scotch and Irish whisky distillates: Bourbons contained less arabinose and more xylose through new wood extractions\textsuperscript{181}. Bourbon spirit had greater total sugar contents than Scotch and Irish (Table IV), and quantitative differences may increase with age. Such concentrations of sugar in retail whiskies are thought too low (Table IV) to induce \textit{sweet}\textsuperscript{138,209} characters – detection threshold is approximately 5 g litre\textsuperscript{-1} in water\textsuperscript{1}. Ethanol, enhancing water structures through hydrophobic effects\textsuperscript{75,230}, decreased sweetness intensity and persistence in sugars\textsuperscript{90}. In summary it is believed that sugars make lesser contributions to \textit{flavour}\textsuperscript{209} than other congeners such as vanillin, whisky lactone and maltol. \textit{Fruity, woody, floral} and \textit{buttery} characters enhances \textit{sweet} characters in whisky\textsuperscript{209}. However, Swan has suggested products of hemicellulose degradations add \textit{fudgey} and \textit{caramel} notes and colour to whisky, those of cellulose have little impact (Swan. \textit{J.}, unpublished).

T.2. \textit{sour}

Wood-derived acids and esters in whiskies are thought to influence \textit{flavour} little\textsuperscript{181}. Wood-derived non-volatile congeners in matured whiskies include: oxalic, fumaric, succinic, methyl- and methoxy succinic, mesaconnic, adipic, pthalic, azelaic, sebacic and trimethylbenzoic acids. New distillate has a fixed acidity of zero\textsuperscript{34} but over 12 months the extraction of acids, oxidations of ethanol and other congeners and other reactions produce an acidic environment\textsuperscript{134}. A typical matured whisky is pH <4.5\textsuperscript{56}.

T.3. \textit{Salty}

This character, often adopted in whisky \textit{flavour} evaluations, is of uncertain origin. It is possibly associated with peat bogs close to a sea, saturated with marine spray and seaweed relics\textsuperscript{141}. Coastal warehousing with permeation evaluations, is of uncertain origin. It is possibly associated with peat bogs close to a sea, saturated with marine spray and seaweed relics\textsuperscript{141}. Coastal warehousing with permeation by damp salty air could produce \textit{Salty} characters\textsuperscript{141}.

T.4. \textit{bitter: see section M (moutheffect) – astringent}

\textbf{M. Mouth effect (mouthfeel)}

M.1. \textit{warming} – alcoholic, burn, fiery
M.2. \textit{coating} – oily, creamy feeling

A highly intense biting sensation, described as \textit{burning}, can increase to a pain sensation. \textit{Burning} also includes a \textit{warm sensation}\textsuperscript{102}.

### TABLE IV. Contents (mg litre⁻¹) of sugars in some whiskies.

<table>
<thead>
<tr>
<th>Sugar</th>
<th>Scotch (6 y)</th>
<th>Scotch (12 y)</th>
<th>Irish</th>
<th>Bourbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glucose</td>
<td>106.0 - 248.3</td>
<td>170.5 - 181.6</td>
<td>114.1</td>
<td>85.1</td>
</tr>
<tr>
<td>Proto-quercitol</td>
<td>10.4 - 16.5</td>
<td>28.9 - 34.4</td>
<td>8.6</td>
<td>90.9</td>
</tr>
<tr>
<td>Arabinose</td>
<td>14.4 - 21.1</td>
<td>35.6 - 42.9</td>
<td>12.4</td>
<td>82.5</td>
</tr>
<tr>
<td>Xylose</td>
<td>6.2 - 8.2</td>
<td>18.4 - 20.1</td>
<td>5.3</td>
<td>82.1</td>
</tr>
<tr>
<td>Mannose</td>
<td>31.3 - 69.6</td>
<td>35.3 - 35.5</td>
<td>6.8</td>
<td>19.2</td>
</tr>
<tr>
<td>Galactose</td>
<td>1.5 - 3.0</td>
<td>5.4 - 6.2</td>
<td>0.7</td>
<td>16.2</td>
</tr>
<tr>
<td>Rhamnose</td>
<td>1.5 - 2.2</td>
<td>4.0 - 4.5</td>
<td>1.5</td>
<td>10.6</td>
</tr>
<tr>
<td>Inositol</td>
<td>1.2 - 2.2</td>
<td>4.4 - 5.6</td>
<td>1.2</td>
<td>13.1</td>
</tr>
</tbody>
</table>

(Nykänen *et al.*, 1984; reproduced with permission from *Helsinki Foundation for Biotechnical & Industrial Fermentation Research*, 1984, 141)
In many products the term *creamyness* is important for appearance, flavour or texture64. In whisky, understanding of the character is limited but related to mouthfeel113 and also described as ‘length in mouth’81. Perception could be related to *thickness*, *smoothness*115 and *fatty mouthfeel*129 and is closely related to *buttery* (diacetyl) in many foods and whisky81, 111, 128, 166. In whisky, consumers to represent maturity may use this character associated with: *smoothness, roundness, body, richness and mellowness*85. Ethyl lactate, from esterification of lactic acid of bacterial origins, is reported linked to *creamy* character229. In spirit, ethyl lactate yield is related to length of fermentation80. However, relationships between *creamy* and *smoothness* appear to differ.

### M.3. Astringent - *drying, furry, powdery*

Astringent is a trigeminal tactile sensation related to behaviour of the epithelium on exposure to tannins yielding on ingestion *drying, roughing, puckering or drawing* sensations126. Such sensations, from binding of tannin to salivary proteins, mucopolysaccharides or directly to oral epithelia, reduce the lubricating effects of saliva, promoting *roughness*, particularly following repeated exposure126.

Such flavour components, absent from new spirit, accumulate through extraction of wood and by oxidation processes. Wood-derived tannic substances contribute *bitter* and *astringent* character, but add *colour* and *delicate fragrance* to whiskies165.

These water-soluble plant polyphenols, are commonly divided into the condensed – derivatives of flavonols – and hydrolysable tannins (gallotannins and ellagitannins). Ellagitannins, monosaccharide polyols (normally D-glucose) with hydroxyl groups esterified by either gallic or hexahydroxydiphenic (HHDP) acids, are hydrolysed either enzymically or in acid or base conditions, to free gallic or HHDP acid, the latter lactonizing to ellagic acid165. Polyphenols from white oak heartwood include gallic and ellagic acids, gallo- and ellagi-tannins37, 177. Such tannins oxidise slowly and polymerise as heart wood ages, reducing solubility165 and perceptions of astringency as in ripening fruit88. The effect is thought to be41: promotion of ethanol oxidation to acetaldehyde and diethyl acetel; and formation of esters from acids (e.g. acetic acid) and alcohols. Tannic substances assist in removal of distillate sulphides95, 165 and nitrogen compounds20. Ellagitannins, abundant in raw wood, in excess confer undesirable flavour characters – contents can be reduced by hot water extractions or charring7, 134. Ellagitannin hydrolyses to gallic and ellagic acids, absent from new distillate64 but present in maturing malt whiskies after 2 years226. Wine spirit extraction of gallic acid is maximal after heat treatment of wood at ca. 165 °C151. Gallic and ellagic acid contents of spirit form indicators of maturation177 but their influences on whisky flavour are not clearly understood165.

### FUTURE RESEARCH

This review treats flavour attributes of whiskies, defined in a revised flavour wheel, as if perceived at a unified time point. However perceptions on ingestion of whisky form a temporal progression and the limited understanding of time intensity features suggest a fertile area for research.

Sensory assessors and panel are not analytical instruments. In assessing products, psychophysics and psychology interplay. Definition and number of attributes and scale usage are important in assessor training; order and session effects should be considered in industrial sensory panel assessments.

Understanding of the fundamental nature of whisky maturaion is also required. Little is known about detailed physical structures of the aqueous ethanol liquid phases of new distillates and matured whiskies. High-resolution analysis strategies, such as neutron scatter, combined with headspace congener studies will contribute to an understanding of sensory quality that will benefit whisky distillers.

However, perhaps greatest priority should be given to understanding perceptions of flavour character in whiskies. Products are perceived holistically by consumers but analysed by sensory assessors through quantifications of deconstructed attributes. Study of relationships between these two, fundamentally different, forms of mental processing is an urgent requirement for understanding whisky quality.

### CONCLUSIONS

On drinking a glass of whisky, consumers employ pattern recognition processes, using sensory data to develop a holistic mental image in specific regions of the brain. Flavour recognition involves matching of information from long-term, short-term and sensory memories. Whisky maturation influences volatile congener release into headspaces through modifications of spirit liquid phases, and agglomerates. Complex changes in congener partitioning replace immature notes in new distillates with matured whisky characters.

The revised flavour wheel specifies a vocabulary that defines consensus deconstructed attributes of whiskies to meet industrial needs. Each attribute is demonstrable by a flavour standard and terms suitable for training of sensory assessors for quality assurance, new product development and similar purposes.

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