

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

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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

Improved congener analyses have not yielded greater understanding of whisky flavour⁵¹: a dynamic interaction²⁰⁹ between individuals and flavour components²⁶⁸. Perceptions of flavour, notes or attributes can be expressed as language^{91,233} but are more commonly used in Gestalt^{65,91,107,161,232,242} 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.

Appreciation of whisky character is a synergistic and holistic perceptual process with extrinsic attributes (branding, labelling, marketing and packaging) important in choice decisions (Fig. 1). A drink is more than the sum of its component perceptions. Sensory assessors generate data relevant to consumer judgements, but utilise different forms of mental processing.

On tasting unlabelled whisky, consumers match perceptions against prior experience, using intrinsic attribute patterns. On a mismatch, individuals move to evaluating small numbers of intrinsic attributes, clusters of individual assessments, with sequential creation of further mental images²⁴². Such processing is modelled in sequential assessor evaluations of attributes in appearance, aroma, taste, mouthfeel and after-taste.

Psychophysics suggests humans have physiological limitations in perceptual ability²³ and can identify no more than three or four flavours notes in mixtures^{119,120,122}. Only this number are held in short-term memory, more

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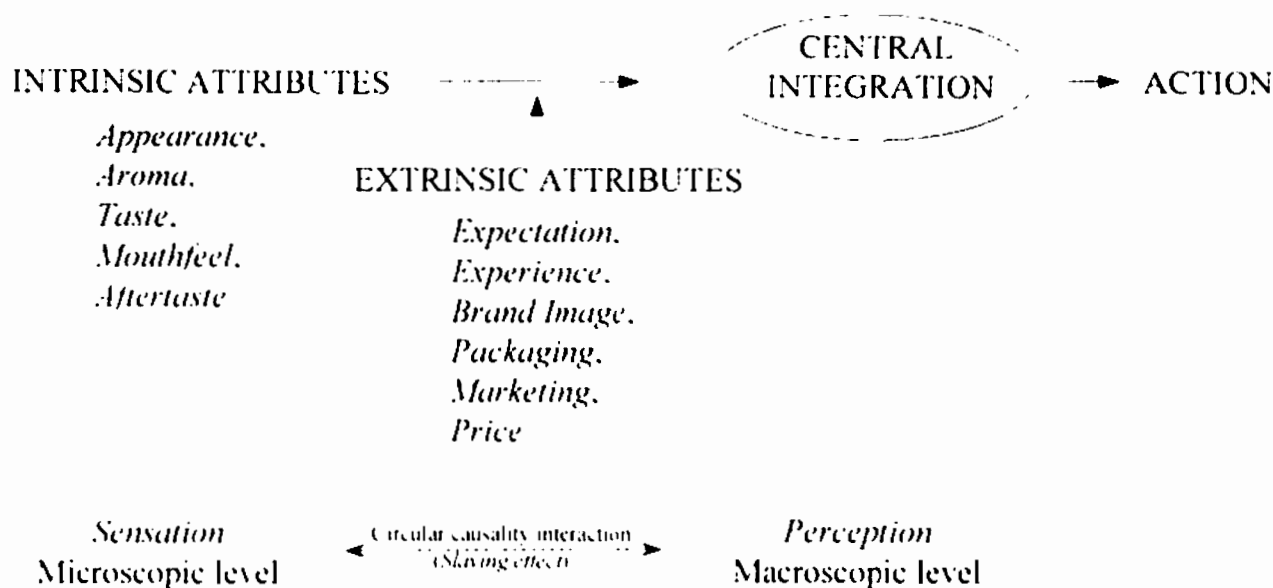


FIG. 1. Intrinsic and extrinsic attributes.

in long-term memory²⁷⁵. Spatial response patterns of flavour component mixtures may thus not be summations of individual flavour notes¹²³.

The beer flavour wheels^{125,157} concentrate assessor attention to specific flavour attributes, including mouthfeel attributes, important in beer. Studies of wood-matured ports⁵² and whisky²⁰² 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^{89,126,187,188}. Processes of odour recognition involve primary visual cortex (BA 17) activity, involving comestibility (suitability for drinking) of products²²⁴.

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 memory²²⁴ 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 recognition²²¹ with collections of stimuli from sensory systems (visual, olfactory, gustatory and chemesthesis),

integrating in specific brain regions to form macroscopic representations²³² of whiskies (Fig. 1).

Research on model and malt whiskies^{46-48,51} suggests wood maturations change partitioning of key flavour components with less desirable flavour notes^{49,50}, increasing retention in liquid phases, recently simulated¹⁴⁸.

Fatty acid ethyl esters, amphiphiles with central polar groups and peripheral hydrophobic aliphatic carbon chains, are important in stabilising whisky headspace compositions²⁰⁸. Structure influences solubility in aqueous ethanol: excess esters form agglomerates²⁵⁵, yielding microemulsions. At 23% (abv), agglomerate diameters increase¹⁹⁰ forming hazes^{90,195}. Chill filtration, prior to bottling, removes excess agglomerates – changing congener composition but not sensory quality²⁰⁸. Agglomerates are dominated by ethyl dodecanoate (laurate, C12), tetradecanoate (myristate, C14) and hexadecanoate (palmitate, C16), contributions determined by aliphatic chain length^{46,48}. Other congeners – alcohols, aldehydes and acids – also contribute to agglomerates⁴⁹, influencing sensory character.

In wood maturations, non-volatile components, including sterols and tannic acids, stabilise ester agglomerates^{48,190}. Temperature influences both agglomerate behaviour and distribution of flavour-active congeners between solution and headspace phases⁵⁰. At oral temperatures, agglomerates suppress volatile congeners more efficiently⁵⁰, but differences between nosing and tasting are thought generally small²⁰². In summary, in agglomerate formation congener activity coefficients are increased by extracted wood components.

Alcohol strength influences congener distribution⁴⁵ 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 thresholds⁴⁵. 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 quality⁴⁵. 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^{82,173,273}. Grain whisky is a product of continuous fractional distillation¹⁸⁶ of fermented wheat and maize¹⁶⁹, saccharified by lightly-kilned barley malts²⁰⁰. 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 impacts¹⁶⁹. Maturations influence final flavour in blends or single whiskies with cask management ensuring product consistency^{31,151,165}.

A REVISED WHISKY FLAVOUR WHEEL FOR SENSORY ANALYSIS

The flavour wheel of Shortreed and coworkers²³³ ordered attributes in classifications based on production.

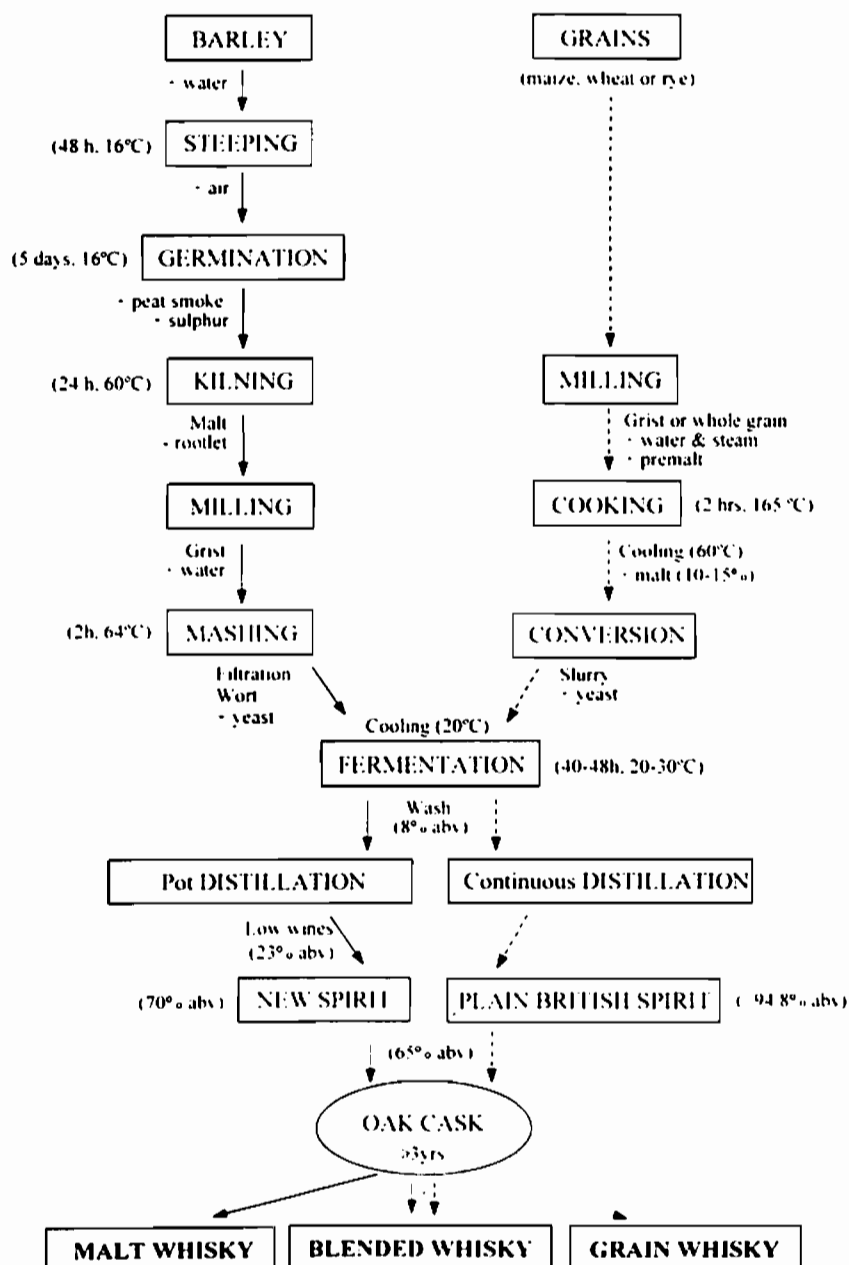


FIG. 2. Production of Scotch whisky.

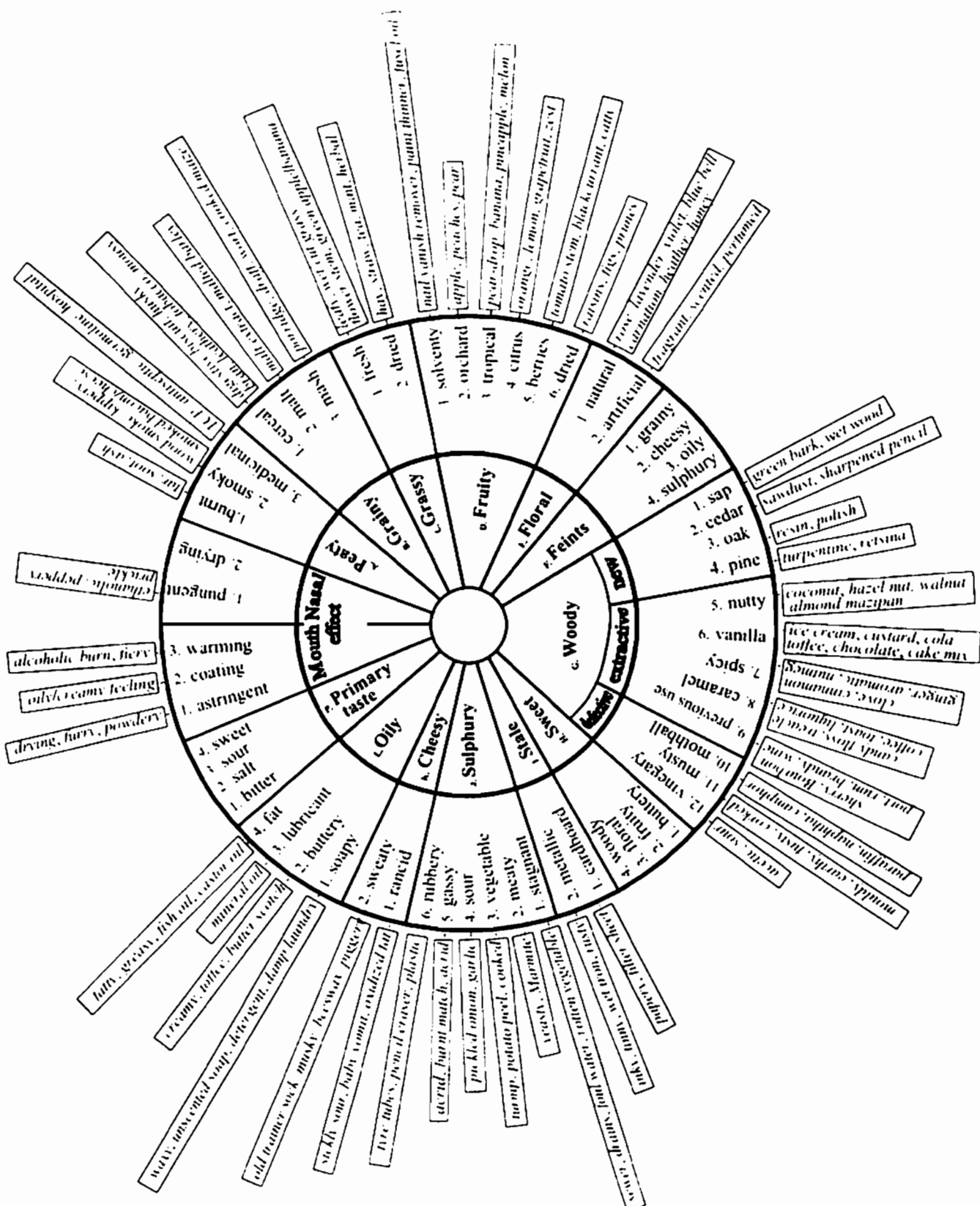


TABLE I. Whisky descriptors and reference compounds.

Code	Flavour Wheel term	Reference compounds for assessor training	Concentration (mg litre ⁻¹)
N.1	<i>Pungent</i>	Formic acid ¹⁹⁹	10 x 10 ³
A.1, 2	<i>Burnt smoky</i>	Guaiacol ¹²⁹	27
A.3	<i>Medicinal</i>	<i>o</i> -Cresol ¹³⁰	1.75
B.2	<i>Malty</i>	Malted barley ¹⁹⁹	-
		2- and 3-Methyl butanal ^{13, 193, 194} , 4-Hydroxy-2(or 5)-ethyl-2(or 5)-methyl-3(2H) furanone ⁹⁴ , 4-hydroxy-2,5-dimethyl-3(2H) furanone ⁹⁴	0.6 (2-methyl butanal) ¹⁵⁵ 1.25 (3-methyl butanal) ¹⁵⁵
C.1	<i>Grassy</i>	Hexanal ¹²⁹	5
		<i>cis</i> -3-Hexene-1-ol ¹⁹⁹	1.00 x 10 ³
D.1	<i>Solventy</i>	Ethyl acetate ¹³⁰	1.12 x 10 ³
		2-Methyl propan-1-ol ¹⁹⁹	1.00 x 10 ³
D.2	<i>Fruity (apple)</i>	Ethyl hexanoate ¹²⁹	2
D.3	<i>Fruity (banana, pear-drop)</i>	<i>iso</i> -Amyl acetate ¹²⁹	7
D.5	<i>Berry</i>	Thiomenthone ¹³⁰	3x 10 ³
	<i>Catty</i>	Thiomenthone ¹³⁰	1.26
		Sodium sulfide · mesityl oxide ¹⁹⁹	100 each
E.1	<i>Floral (Natural - rose)</i>	Phenyl ethanol ¹²⁹	1.52 x 10 ³
	<i>- violet</i>	α -, β -Ionone ⁵⁴	>3x10 ⁻³
	<i>Floral (Artificial - scented, perfumed)</i>	Geraniol ¹²⁹	19
G.5	<i>Nutty (coconut)</i>	Whisky lactone ¹²⁹	266
	<i>marzipan</i>	Furfural ¹²⁹	839
G.6	<i>Vanilla</i>	Vanillin ¹²⁹	43
G.7	<i>Spicy</i>	4-Vinyl guaiacol ¹²⁹	71
	<i>Spicy (clove)</i>	Eugenol ^{129,199}	1 - 55
G.8	<i>Caramel (candy floss)</i>	Maltol ¹²⁹	1.14 x 10 ³
G.10	<i>Mothball</i>	Naphthalene	>8x10 ⁻³

G.11	<i>Mouldy</i>	2,4,6-Trichloroanisole ¹⁹⁹	10
	<i>Earthy, musty</i>	Geosmin, 2-methyl <i>iso</i> -borneol ^{237, 69}	-
G.12	<i>Vinegary</i>	Acetic acid ¹²⁹	5.32 x 10 ³
I.1	<i>Cardboard</i>	2-Nonenal ¹³⁰	0.08
J.1.6	<i>Stagnant, rubbery</i>	Dimethyl tri-sulphide (DMTS) ¹²⁸	3
J.2	<i>Yeasty</i>	Hydrogen sulphide (H ₂ S) ¹²⁸	> 0.02
	<i>Rotten egg</i>	Hydrogen sulphide ¹²⁸	> 0.14
	<i>Meaty</i>	Methyl (2-methyl-3-furyl) disulphides ²⁷	-
J.3	<i>Vegetable (sweet corn, cooked cabbage)</i>	Dimethyl sulphide (DMS) ¹²⁸	> 0.6
J.5	<i>Gassy</i>	Ethanethiol ¹²⁸	> 0.072
		3-Methyl-2-butene-1-thiol ¹²⁸	> 7.2 x 10 ⁻⁴
k.1	<i>Rancid</i>	<i>n</i> -Butyric acid/ ethyl butyrate ²⁶	>2
	<i>Sweaty</i>	<i>iso</i> -Valeric acid ¹²⁹	2
L.	<i>Oily</i>	Heptanol ¹⁹⁹	1
L.1	<i>Soapy</i>	Ethyl laurate ¹²⁹	12
		1-Decanol ¹⁹⁹	100
L.2	<i>Buttery</i>	Diacetyl ¹²⁹	0.1

(199) - 23% ethanol solution; (129) - in 23% grain whisky; (128) - in lager; (26, 27, 54, 69, 94, 130, 199, 237) - > threshold; (155) - threshold in beer

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^{157,179}, 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 whisky¹²⁹ more often use subtler terms. For assessor training, reference compounds are recommended (Table 1): formulations with cyclodextrins 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 endings²⁸¹ – *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 contributes²⁸¹. The off-note *peppery-pungency* originates in bacterial, notably *Lactobacillus*^{105,138,160,241} spp., fermentations producing acrolein^{105,160}, at elevated temperatures or in extended fermentations²⁴¹, from glycerol from yeast catabolism. The product, β-hydroxy propionaldehyde, is in distillation³⁸ degraded to lachrymatory acrolein – inducing *pungent, burnt and peppery* notes⁹⁰, *red eyes*¹⁶⁰. Wooden washbacks

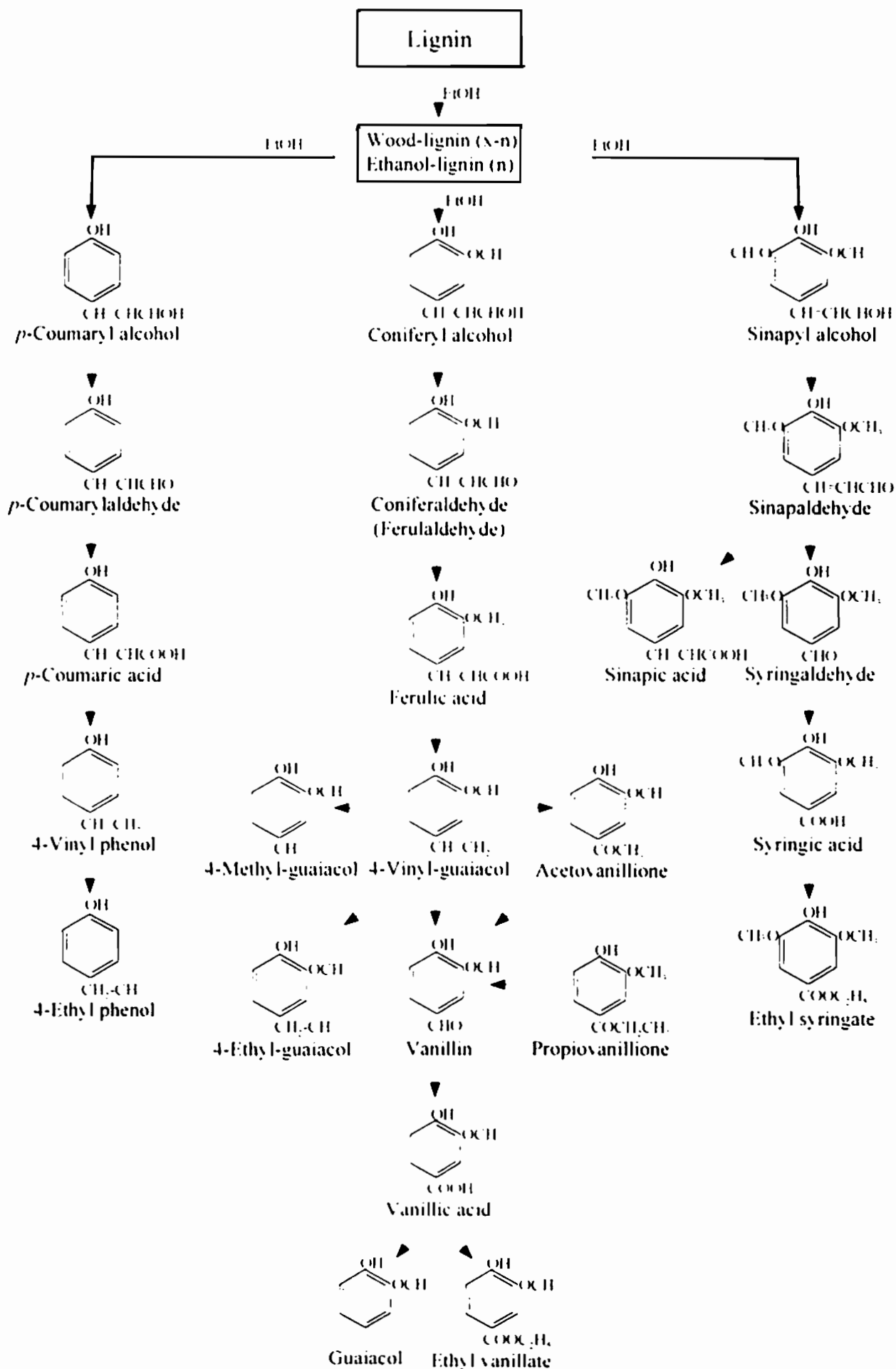


FIG. 4. Lignin-derived aromatic aldehyde transformations in whisky.

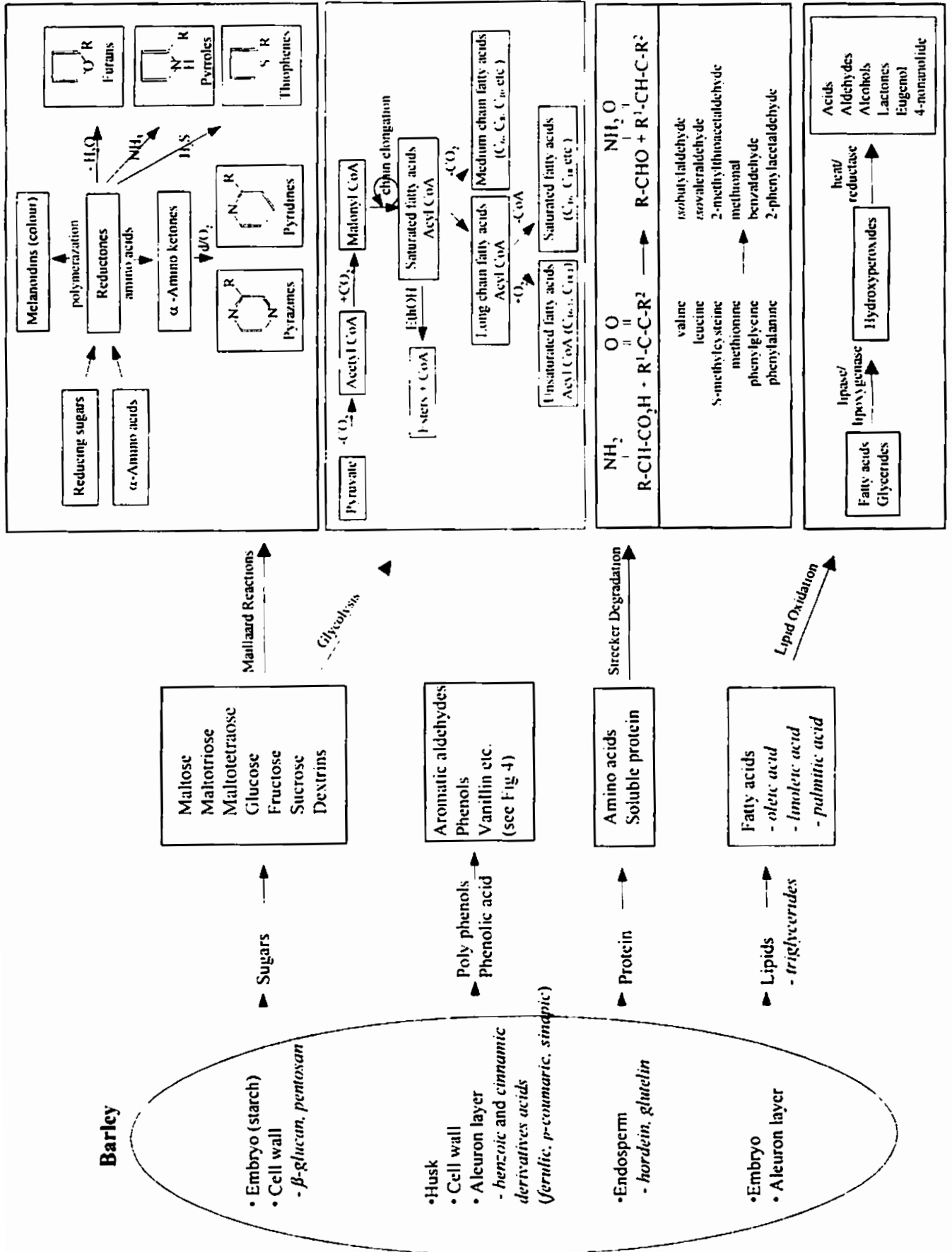


FIG. 5. Transformation of flavour constituents of barley during whisky production.

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are sources of bacterial contamination but pH, oxygen tension, agitation, presence of yeast cells and/or mash residue, fermentable sugars and glycerol influence acrolein production¹⁶⁰. After 2–3 maturation years, these off-flavours disappear: acrolein reacts with ethanol yielding 1,1-diethoxy-2-propene^{38,138}, 1,1,3-triethoxypropane, 3-ethoxypropionaldehyde and propene^{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, smoked bacon/cheese*
- A.3. *medicinal – TCP, antiseptic, germoline, hospital*

Smoky is linked to degraded wood carbohydrates – cellulose, hemicelluloses and lignins³⁷. *Peaty* attributes originate in smoke, introduced into the airflow during the kilning processes^{11,12}, from phenolic compounds²⁸⁰ and also sulphur- and nitrogen congeners, pyridines and thiazoles. Quantitatively important are phenol, cresols (*m*-, *o*-, *p*-), xylenols, and *p*- and *m*-ethylphenol. Guaiacol has low flavour thresholds (3 µg litre⁻¹ in 10% spirit⁶⁶; detection, 0.09 µg litre⁻¹ and recognition 3 µg litre⁻¹¹²⁷) and substituted methoxy phenols²⁷⁸ have significant flavour impacts. Important volatiles for desirable smoke flavour are abundant in phenolic and basic subfractions, acidic and neutral are of secondary importance³⁷.

Although kilning uses alternative fuels, inclusion of short-time intensive peat combustion yields a characteristic *reek*. Smoke absorption is maximal at 15–30% moisture in malting barley¹¹. Raising kilning from 400 to 750°C yields several-fold increases in phenol and cresol, reducing guaiacol¹¹. Thomson²⁵⁷ has reviewed relationships between flavour-active phenols, peat composition and kilning. Charring stave surfaces introduces *smoky* attributes following extraction of thermally degraded lignins (Fig. 4) with ethanolysis of Braun's lignin¹⁷⁶. The resulting aromatic aldehydes induce *sweetness* and *smoky* attributes^{43,44}. Other phenolics – e.g. benzoic, cinnamic, ferulic (4-hydroxy-3-methoxycinnamic)⁹⁹, *p*-coumaric (4-hydroxycinnamic) and sinapic acids – originated in cereal cell walls (Fig. 5) and are transformed into phenols by kilning, thermal decarboxylations²⁶¹. Ferulic and *p*-coumaric acids yield 4-vinyl guaiacol and 4-ethyl phenols, respectively (Fig. 4), through yeast decarboxylations^{36,59,66,243}, particularly in spirits from rye abundant in phenolic acids¹⁸⁹.

Hydrophilicity in phenols ensures feint retention limiting final whisky concentration^{98,189}. Phenol dominates (46–67%) in peated barley malt, cresols

(58–61%) final spirit. Both, from peated malts, influence character of Scotch, Spanish and Japanese whiskies⁶⁷. *O*-cresol is most abundant in Scotch whisky with thresholds of 31 mg litre⁻¹ in 10% spirit⁶⁶ and 30 and 120 µg litre⁻¹ (detection and recognition) in 23% grain whisky¹²⁷. Phenol contributes only *circa* 7% odour units^{16,225}, but related attributes are important, especially in Scotch whisky²⁸⁰ with characters often described as *medicinal* and *iodine*²³. In Speyside malts this is more often *peaty*. Strong phenolic characters such as *medicinal* relate to kilning *o*- and *m*-cresols, *peaty* may be linked to eugenol²⁵⁰. In Bourbon and Canadian whiskies unpeated, green malts from barley, corn or rye, and phenol and cresols have lesser impacts on character and *smoky* attributes originate in lignin breakdown components. These included eugenol, 4-ethyl phenol and 4-ethyl guaiacol, from new staves after charring and ethanolic extractions¹³¹ (Fig. 4) or cereal cell walls. Eugenol with low thresholds of 11⁶⁶, and detection at 0.5 and recognition of 5 µg litre⁻¹¹²⁷, influences Bourbon flavour⁶⁶. Adding phenol mixtures to Bourbon mimicked Scotch whisky characters of *woody* with additional *oily*, but not *estery* and *sweet* attributes⁶⁶.

Humic and fulvic acids in mashing waters^{172,272} influence *peaty* characters. Congeners including halogens of marine origins¹⁷² and microbial activity also generates highly flavour-active compounds such as chloroguaiacols that at extreme dilutions yield distinctive off-notes, e.g. *Rio* character in coffee^{55,146,240}.

In the original flavour wheel²³³, discrimination of phenolic attributes was contentious with secondary tier clustering of *medicinal*, *peaty* and *kippery*. Relationships between the stronger *medicinal*, and *peaty* are unclear^{12,250} as are those between *peaty* and *dry* attributes in whiskies¹⁷¹. No relationship between *dryness* of Scotch and total phenol content has been demonstrated^{12,251}. Interestingly, a specific volatile phenol anosmia – partial odour blindness – is reported in 15% of the UK population for suggesting inconsistent flavour influences⁹⁸.

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 *fruity*, *hay-like*, and *damp-straw* notes, replaced by *burnt*, *bready*, *malty* and *chocolate-like* notes¹⁴ with increased kilning temperatures. Maillard browning intermediates interact with cereal lipid oxidation products (Fig. 5).

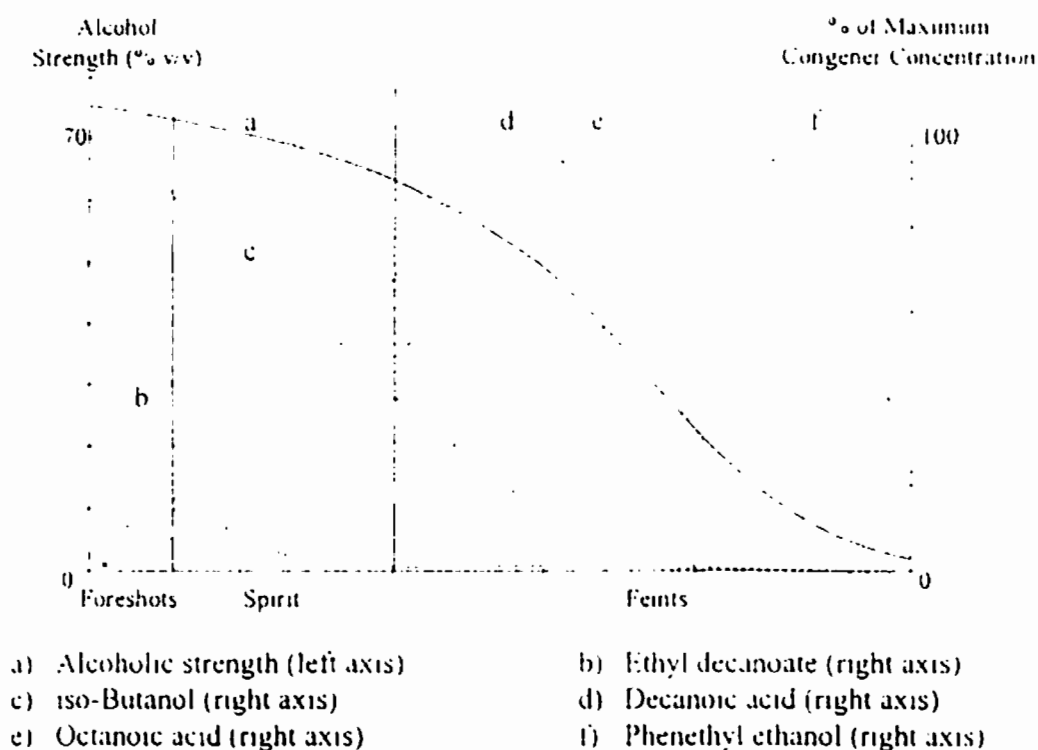


FIG. 6. Fractional distillation – Foreshots, Spirit, Feints – and profiling of alcoholic strength and five whisky congeners during a laboratory spirit distillation (Goodall, *et al.*, 1999; reproduced with permission from *Institute of Brewing*, 1999, 105).

Furfural, *grainy* at 20–30 mg/litre in Scotch whisky¹³⁸, 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^{12,17,176,338} (Fig. 5): concentrations are functions of wash pH especially with high numbers of lactic bacteria¹⁷.

In whole and ground cereals²²⁹, aldehydes, enals, 2,3-butanediols, acetic acid, and chloro- and bromo-methoxybenzenes dominate volatiles. The last is associated with *musty* in sorghums. In malts¹³ *malty* is associated with 2- and 3-methylbutanal, linked to *worty* in alcohol-free beer^{193,194}. Perpète and Collin^{193,194} associated *worty* primarily with 3-methylthio-propionaldehyde but other compounds influencing *malty* or *cereal-like* character include ethylmethyl-pyrazines, maltol¹³ and hydroxydimethylfuranone from 2-methylpropanal⁷¹. 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*⁹⁴ 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* attributes²³³ 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 usage²³³ and multifaceted in perfumery¹⁰². *Grassy* notes from hexanal are perceived *almond* by a minority (12%) of assessors¹²⁹.

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* notes¹⁵⁶. Aldehydes originate in barley lipids, dominated by 9,12-octadecadienoic (linoleic), 9,12,15- octadecatrienoic (linolenic) and 9-octadecenoic (oleic) acids. Malt lipoxygenases oxidise linolenic and 6,10,14,18-eicosatetraenoic (arachidonic) acids (Fig. 5), yielding 9- and 13-hydroperoxides and further aldehydes: hexanal, trans-2-hexenal¹⁸⁹, 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)¹⁷⁵.

Estery characters

Estery characters are ordered as in the original wheel²³³, and include *solventy*, *fruity*, *floral*, and *feinty*, functions of aliphatic chain length²¹⁹. In distillations, *solventy* and *fruity*, are related to heads (foreshot), passing to *floral* and *feints* (tails) as distillation proceeds^{66,189}

(Fig. 6). Spirit cut-off points are central to *estery* characters^{173,189} and differ between distilleries. Although individual esters showed less impacts on whisky flavour, in total, esters form a key component of flavour²²⁵, contributing particularly to complex *roundness*²⁵¹.

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 concentrations¹⁸⁹ (Fig. 5). Effective concentrations vary: ethyl caproate (C6) is released into wash, laurate (C12) largely retained within yeast cells¹⁸⁰. Fermentation ester formation is influenced by wort gravity²¹⁵, yeast strain⁹³ and pitching rate^{116,214}, wort unsaturated fatty acid concentration^{18,138,259}, aeration^{18,259} and temperature¹⁵⁹. Mass transfer of substrates, and yeast growth, are key factors for wort levels of medium-chain fatty acids¹⁸.

In maturation, further esterification of fatty acids²¹⁶ occurs, and ethyl acetate¹⁷⁷ becomes abundant originating in acetic acid from hydrolysis of hemicellulose acetyl groups¹⁷⁶, oxidation of ethanol, and wood charring³⁷. 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 maturation and others – ethyl decanoate (caprate, C10), hexadecanoate (palmitate, C16) and 9,12,15-octadecatrienoate (linoleate: C18) – show significant reverse reactions^{177,216}.

The first-light fraction (foreshots)

D. Fruity characters

- D.1. *solventy* – 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 whisky¹⁸ – are often perceived *solvent-like*. Ethyl acetate has high thresholds of between 331⁵⁶ and 74 mg litre⁻¹¹⁹⁵ with detection and recognition thresholds in 23% (abv) grain spirit of 14 and 100 mg litre⁻¹, respectively¹²⁷. However, esters show synergistic and suppression effects that could influence overall character²⁰¹.

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* characters¹⁷³.

Dried-fruity notes in dried bell peppers¹³⁷ are linked with 2-methylpropanal, and 2- and 3-methylbutanal, also linked to *malty* and *worty* notes^{13,193,194} 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 flavour²²⁵. Ethyl hexanoate (caproate, C6) imparts *fruity (apply)* characters and with increasing ester chain length *soapy, oily* and *sour* notes, related to whisky immaturity^{40,205}. 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* in distillates, often discarded as tails⁸⁷. Excess higher fatty acid esters (>C₁₆) cause chill haze in spirit reductions to bottling strength^{173,208} and are less desirable in new distillates^{41,82} (Fig. 6). Yeast in wash at distillation enhances concentrations²⁴⁵. Propanol, *iso*-butanol, amyl and *iso*-amyl alcohols are present in head and feints fraction. *Feints* notes, infrequent in early spirit fractions¹⁶⁸, are linked to certain fatty acids and sulphur congeners (e.g. dimethyl trisulphide) in tails¹⁶⁸.

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^{57,58}, imparts *fragrant* with dilution to 23% (abv)¹⁹⁵. This β -damascenone has a high odour unit value (2500) in whisky, but low intensity index limits detection¹⁹⁵. Autoxidation of vitamin A or lipids, from yeast or barley⁵⁴, and breakdown of oak norisoprenoids⁴¹ 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 quality¹⁷². Notes include *leathery* or *cereal-like (cooked mash, biscuity)* passing

to *sweaty (piggery)* and into *stale fish* characters²³³. *Sweaty* is related to *isovaleric acid* content¹⁶⁸. Feints, with distinctive *stale* notes and *metallic* aftertaste¹¹, have abundant malt-derived phenols and DMTS²⁷.

Maturation characters

G. Woody character

White oak wood (*e.g. Quercus alba*) varies in contents³⁷ 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 compounds¹⁷⁷. Heartwood contain more lipids: triglycerides of C₁₈ unsaturated and C₁₆ saturated fatty acids, sterols and a ferulic acid ester with a C₄₀ wax alcohol²³⁸. All have **gradual impacts** with cask ageing and sterols producing hazes during spirit reduction for bottling²³⁸.

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 extractives influence flavour²³⁸ conferring *smoky*³⁷ and *woody* characters. In charring lignins are more stable than polysaccharides³⁷. In acidic (~pH 4.5) wood maturations¹⁷⁶ insoluble hemicelluloses slowly depolymerise and are extracted.

Woody characters are complex in both whisky and wines¹⁷⁸. 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 coworkers¹⁹² regarded *cis*- and *trans*-lactones, eugenol, vanillin and syringaldehyde as the volatiles with greatest sensory impact with optima for extractions of vanillin and syringaldehyde of 165–215 °C¹⁵¹. A syringaldehyde/vanillin ratio of 1.4/2.5 indicates balanced decomposition of oak lignin¹⁹⁷. Interactions between certain lactones and vanillin are important at concentrations present in Scotch whisky enhancing vanilla character (Swan, J., unpublished). Certain wood phenolics, notably vanillin (3-formyl-2-methoxyphenol), syringaldehyde and 5-hydroxy methyl-2-furfuraldehyde are markers of good spirit quality. The origins appear desirable staves with abundant earlywood with many annual rings cm⁻¹ (maximum 12)²¹⁸.

Nykänen¹⁸¹ concluded that hydrolysis of lignin-hemicellulose complexes was more important than ethanolysis as caskwood absorbs water in preference to

ethanol. However, ethanol activity is maximal at cask strength (60% abv). This enhances solubility of key congeners, acids and phenolics that with derived oxidation products, confer important characters – *maturity, roundness, well-balanced* and *smooth*¹¹². *Woody* attributes are subdivided into: new wood, extractive and defective staves.

New wood characters

- G.1. *sap – green bark, wet wood*
- G.2. *cedar – sawdust, cardboard, sharpened pencil*
- G.3. *oak – resin, polish*
- G.4. *pine – turpentine, retsina*

Fresh sawdust or *sap* notes originating in new barrels, are related to wood origin, and eliminated with second useage³². In wines³², unpleasant *sawdust* notes are linked to (E)-2-nonenal (*rancid* in beer^{10,262}), 3-octen-1-one, (E)-2-octenal and 1-decanal. These compounds, associated with *cardboard* in whiskies¹³⁰ and other products^{196,277}, originate in linoleic acid oxidation⁹ in unsaturated barley lipids. Cask toasting processes reduce (E)-2-octenal, and associated notes, in matured wines³².

Higher alcoholic strength fillings reduce extraction of wood-derived components and associated notes²³⁸. In an 8-year old whisky, filled at 59% abv, character was *flavoured*, at 63% *less matured* and *weaker* and at 77% *green oak*^{177,238}. 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% abv²⁴. For balanced extractions the optimum was 50–55% abv²⁴, typical of armagnac.

Wood extractive characters

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

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⁻¹) and *oak wood-like* at lower (0.1 mg litre⁻¹)^{139,231}. This lactone, together with 4-nonanolide and eugenol^{66,154}, are major volatile congeners derived solely from oak^{142,238}. A possible lactone precursor is 2-methyl-3-(3,4-dihydroxy-5-methoxybenzo)-octanoic acid^{152,183}.

Four lactone isomers are, *cis*-(3*R*,4*R*), *cis*-(3*S*,4*S*), *trans*-(3*S*,4*R*) and *trans*-(3*R*,4*S*), differing in flavour character (Table II)⁸³. Oak contains only *cis*-(3*S*,4*S*) and *trans*-(3*S*,4*R*)^{152,153}; other isomers indicate synthetic lactones in flavouring/ageing agents^{143,164}. Misidentification of isomers^{21,110,142,149,184} has produced contradictory *cis:trans* ratios, and threshold values^{33,142,163,184}.

TABLE II. Taste and odour properties of oak lactones.

Compound	Taste	Odour
<i>cis</i> -(3 <i>R</i> ,4 <i>R</i>)	<i>Creamy, coconut</i>	<i>Sweet, woody, coconut</i>
<i>cis</i> -(3 <i>S</i> ,4 <i>S</i>)	<i>Spicy, coconut-like</i>	<i>Light coconut, musty, hay</i>
<i>trans</i> -(3 <i>S</i> ,4 <i>R</i>)	<i>Coconut-like, sweet, creamy, fatty</i>	<i>Spicy, celery, slight coconut, green walnut</i>
<i>trans</i> -(3 <i>R</i> ,4 <i>S</i>)	<i>Spicy</i>	<i>Coconut, celery</i>

(Günther et al., 1986; reproduced with permission from *Liebigs 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 whisky¹²⁷ but 0.05 mg litre⁻¹²²⁵ in 34% abv grain spirit; in white and red wines 120 and 125 µg litre⁻¹³⁴. Reported difference thresholds are 241 mg litre⁻¹ in white, 853 in red wine and 75 in 12% abv ethanol²⁰⁴. In white wine lactone confers *musty* notes, in red *harsh* and in 12% ethanol *coconut*, *woody* and *oaky*²⁰⁴ 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*¹⁶⁴. Wood origins can be related to lactone ratio¹⁹², reported⁸⁴ 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 Sessile¹⁵². Ratios (*cis:trans*) also vary through single staves, with *cis* maximal (250 mg kg⁻¹ of wood), and more extractable¹⁴³, at 5 mm below stave surface and *trans* maximal (48 mg kg⁻¹) at 15 mm depth⁴⁴.

Lactones have been studied extensively as important in wine characters^{1,204}. Waterhouse and coworkers²⁷¹ 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 lipids¹⁴² than sapwood: two 3-oxo-retro- α -ionol isomers serve as markers. However, eugenol and vanillin concentrations are similar in American and European oaks³¹. 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 wine³¹. 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 usage⁴⁴. “Standard” Scotch whisky have been reported containing 0.96, “premium” 1.16, and a “high” had 2.17 mg litre⁻¹ total lactone¹⁸⁴. Similar correlations between lactone concentrations and quality grade exist in cognacs¹⁸⁴. There is conversion of *trans* to more stable, flavour-active *cis* form in bottle maturation of wine³⁵.

Thermal lipid oxidations¹⁴² in cask charring increases lactone up to three-fold but excess temperatures reduce surface content^{33,143}. Lactone is retained deeper in staves, and below chars. Care during charring is beneficial as changes in *cis/trans* ratio will influence character¹⁴³. In wines (e.g Chardonnay), green oak yields *vanilla*, *buttery*, *nutty*, *caramel*, *cedar*, *coconut*, *raisin* and *dill* notes, and increases *spicy* characters²²⁷. In contrast, seasoned wood increases *cedar* and *nutty* notes, decreasing *raisin*^{74,227}.

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 whisky²⁶⁹. Certain yeasts, notably *Sporobolomyces*, in specific wines and flor sherries, excrete 4-decanolide and *cis*-6-dodecen-4-olide^{18,167}.

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

Vanilla, often described *chocolate* and *cola* through “circle minded” associations¹⁰², is important in certain whiskies. New casks are toasted to eliminate *new-wood* notes and *astringent* tastes, with an optimum of 165–215°C¹⁵¹ for Bourbons. Charring increases contents of vanillin, vanillic acid and related compounds – acetovanillone and propiovanillone, and other lignin aldehydes – coniferaldehyde, sinapaldehyde, acetosyringone – and their acids¹⁷⁷. Aldehydes are oxidised to acids or converted to vanillin and syringaldehyde contributing to *vanilla* (Fig. 4)^{176,177} with effects^{40,50,176,217} including synergistic interactions (Table III)¹³⁹. Clyne⁴⁰ linked increased vanillin and syringaldehyde in whisky from charred casks with *smooth*, *vanillin*, *sweet*, *malty*, *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*, *meaty*, and *fishy* notes. Gallic acid from tannin hydrolysis is most abundant in uncharred woods, in Scotch whisky the flavour impact

TABLE III. Synergistic effects of aromatic aldehydes in 40% abv.

Compounds	Taste threshold (mg/litre)
Vanillin (V)	0.1
Syringaldehyde (Y)	15
Sinapaldehyde (I)	50
Ferulic acid (FA)	30
Vanillic acid (VA)	25
Syringic acid (YA)	10
Sinapic acid (IA)	100
V/Y	2
FA/VA/YA/IA/V	4
FA/VA/YA/V/Y/I	2

(Maga J.A., 1984; reproduced with permission from *Elsevier Science*, 1984, 409)

of syringaldehyde (50% of total aldehydes) and vanillin (24%)^{44,132,151,217} is thought greater. Increased dissolved oxygen yields higher concentrations of vanillin, syringaldehyde, coniferaldehyde, vanillic and syringic acids^{139,176,217,261}. 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^{43,238}.

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^{145,238}. These sensorially-important phenols are maximal at 5 mm below the char in new wood⁴⁴ with syringaldehyde and syringic acid more abundant than vanillin and vanillic acid. Oak wood drying (air or kiln) also influences vanillin, coniferaldehyde and syringaldehyde contents²⁷⁰. Air seasoning may increase mycoflora attacking cell wall lignins and polysaccharides²⁷⁰, yielding compounds associated with positive maturation characters²⁵².

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

Woody spicy attributes originate in wood extracts, particularly eugenol, derived from lipid oxidation (Fig. 5)^{142,164,165}, abundant in Bourbon whisky^{68,206}. This congener has a thresholds 2–34 µg litre⁻¹ in beers¹⁵⁸, 11 and 50 µg litre⁻¹ in 10 and 20% ethanol respectively²³⁸ and detection and recognition thresholds of 0.5 and 4.9 mg litre⁻¹ respectively in 23% abv grain spirit¹³⁰. 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)^{238,279}. The yeast enzyme ferulic acid decarboxylase⁵⁹ converts cell wall ferulic acid to 4-vinyl guaiacol. The related *clove* has a character linked to *oakiness*²³⁸. However *spicy* notes are common to clove, cinnamon bark oils, and other spices¹⁰² and distinctions may be difficult¹²⁹ 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-methoxy phenol), 4-acetyl-guaiacol and syringol (2,6-dimethoxy phenol), homologues and derivatives. The stability of lignin polymers limits their contributions to maturing spirit⁴³ 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 hydroxymethyl-pyranones²¹⁸ from ageing in freshly charred casks. Caramel added to enhance colour in blended whiskies also contains 5-hydroxymethyl-2-furfuraldehyde¹⁰⁰. In Bourbon whiskey, 2-hydroxy-3-methyl-2-cyclopentenone and 3-hydroxy-2-methyl-4-pyrone (maltol), with *sweet* and *burnt* notes^{176,177}, are important.

Other stove 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 pyrans^{40,41,142,177,210}. 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 *earthy*^{210,263}, but also *phenolic*, *nutty* and *green*. Flavour notes are enhanced when methoxyl groups are present on pyrazine derivatives⁹⁵. Unlike pyrazines, pyridines are perceived as less pleasant: *astringent*, *bitter*, *buttery*, *caramel*, *roasted*, *green*, *earthy*, *rubbery*, and *fatty*¹⁴⁴, and *pungent*, *solvent* and *fishy*⁶⁰. 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 low^{56,210}.

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, barrels^{31,164} 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 maturations, with formation of ethanol cluster structures^{2,3,177}. Such clusters can be deduced from differential scanning calorimetry (Fig. 7)¹¹² and adiabatic expansion studies under vacuum^{79,174} of immature and mature whiskies. Non-volatile oakwood extracts (Fig. 7)^{114,177} stabilise clusters, increasing *mellowness* and *roundness* with accumulation^{40,205,206}. Such non-volatiles are monosaccharides (pentoses and hexoses) and aromatics from cask cell 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

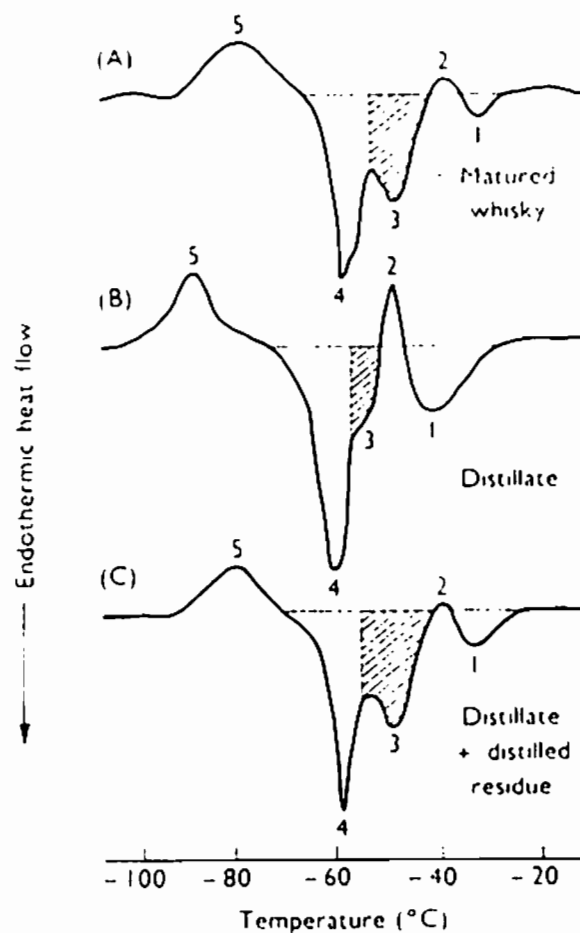


FIG. 7. DSC thermograms of the melting of rapidly frozen matured whisky, distillate of matured whisky and restored whisky (Nishimura, *et al*, 1983; reproduced with permission from Piggott, J. R. (ed.) *Flavour of Distilled Beverages: Origin and Development*, Ellis Horwood, Chichester, p.252).

cork closures, notably *Armillaria mellen*^{222,228,236,237} on corks. In wines such aroma notes are linked to methyl thiopyrazine, 2-acetyl piperidine and its isomer 2-acetyl tetra hydro 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 wines^{28,29,77,118} 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)¹³⁶, introduced in water^{136,220}, 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 *sweet* 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 character¹⁰². 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*, *iso*-amyl acetate was described as *pear-drop* (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 threshold¹²⁹. 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^{18,62}.

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-nonadienal and 2,4-decadienal responsible for *cardboard* in boiled potato¹⁹⁶. Hexadecenoic (palmitoleic) acid autoxidation

yields (E)- and (Z)-2-nonenal and (E)-2-octenal with *cardboard* notes in butter oil²⁷⁷. (E)-2-nonenal in 23% abv grain whisky was described as *cardboard* with detection and recognition thresholds of 3 and 8 µg litre⁻¹, respectively¹³⁰.

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^{76,133,153}, although low concentrations in beers enhance acceptability¹⁸. Water dilutions enhanced flavour impact through hydrophobicity, although such volatility is suppressed by wood-derived congeners²⁰⁷. 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^{7,18,156}. 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 significant⁷. In lagers, ethanethiol evokes stronger *gunpowder* and *acid* notes¹²⁸. In 23% grain whisky detection and recognition thresholds of dimethyl trisulphide (DMTS) were 4 and 20 µg litre⁻¹, respectively¹³⁰, and 3–6 µg litre⁻¹¹³³. In beer associated flavour notes are *garlic* (*onion*, *cabbage*), *drains* and (*struck*) *match*¹²⁸ and thresholds for H₂S are 6 µg litre⁻¹⁹². 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-methylthiofuran. 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 spirit²⁷. Other compounds derived from thiamine and amino acids also have low thresholds, <1 µg litre⁻¹, and are important in roasted coffee²⁶⁰ and yeast extracts⁵.

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 distillation⁷⁸ possibly from thermally degradation of yeast metabolic products such as S-methyl-methionine through Strecker degradation to methional (Fig. 5) and methanethiol⁷⁸. Dimethyl disulphide (DMDS) and trisulphide (DMTS) in new spirit are linearly correlated with wash methional

although DMTS concentration can be modulated in still operation^{76,211}. Malathion used for pest control on barley might influence sulphur congener concentrations, but was reported to have no influence on final spirit²⁵⁶.

Addition of rock sulphur or gaseous sulphur dioxide (SO₂) during malt kilning reduces nitrosodimethylamine (NDMA) level through reactions between barley amines (especially hordeins in the rootlet) and fuel NO₂. Most nitrosamines are unstable, evaporating before the kilning 'break point'. Formation of NDMA is reduced by prior rootlet removal but influenced by hordein content²³⁹. Sulphur dioxide at 10–30 mg litre⁻¹ also reduces malt microbial loads^{11,72,235} and lightens colour. Wort pH is influenced by concentrations of SO₂ and sulphuric acid with effects on polysaccharide, glyco-proteins and glycolipid hydrolysis and wort concentrations of protein, α -amino nitrogen, lipids and fatty acids²³⁴.

Malt yields DMS from S-methyl-methionine (SMM), absent from barley grain but increasing during germination²⁷⁴. 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 (DMSO₂)^{7,76}. Other sulphur congeners formed in mashing include carbonyl and hydrogen sulphides, methanethiol, carbon disulphide, sulphur dioxide and DMS²²³.

In fermentation, DMSO is reduced to DMS by sulphhydryl compounds during the fermentation. Anaerobic bacteria (*Enterobacteriaceae*) in certain washes also produce DMS from DMSO²⁸². Yeast autolysis yields DMDS, DMTS and certain other sulphur congeners^{18,211,244} at concentrations related to duration and intensity of wort heating. Yeast malic and citric acids¹³⁸ promote hydrogen sulphide and sulphur-containing compounds secretion by lactic acid bacteria (*Lactobacillus brevis*, and *L. fermentum*)^{6,138}. Yeast metabolism also has a role, with storage at 5°C yielding less sulphur congeners than 20°C¹⁶². Whisky mashes are susceptible to yeast infections, producing sulphides and further metabolic products (e.g. ethanethiol) through hydrogen sulphide reactions with ethanol¹⁸. Strecker degradations (Fig. 5) of cysteine with diketone yield hydrogen sulphide (H₂S) during fermentation, converted to ethanethiol and diethyl disulphide during distillation²⁴⁴. Such H₂S (typically at 9 mg litre⁻¹) interacts with residual maltotriose (0.8–1.4 mM) during distillation, yielding DMDS from methionine independent of the presence of copper ions⁷⁸. Notes from H₂S were *rotten-egg* at high concentrations (ca 140 μ g litre⁻¹)¹²⁸ and yeasty at 50 μ g litre⁻¹²⁵⁸. Supply of oxygen at distillation has little influence on sulphur compound formation as foam and carbon dioxide replace air in wash headspaces⁷⁸.

Copper interacts with sulphur compounds¹³³ and reaction with copper ions is regarded as essential for producing clean spirit^{173,273}. Copper ions accumulate during wash distillation reaching 15 mg litre⁻¹^{78,213}. Cupric ions react with methional to produce DMDS, converted to other compounds as distillation progresses⁷⁸. As conversion is faster than formation⁷⁸, total DMDS concentrations in spirit are reduced.

Copper sulphate removes volatile sulphur congeners as non-volatile copper sulphides and mercaptides⁸². Still deposits contain copper cyanides, thiocyanates, oxides and sulphates¹⁴⁰. This behaviour may be important for understanding spirit quality⁸². Thiols react with surface copper oxide to form copper thiolates that in excess form complexes becoming self-assembled layers, with chemisorption¹⁰⁹. Thiolate layers react with congeners (e.g. thiophene) influencing sensory quality⁸². However, chemisorbed thiol is limited (<4% of offered thiol concentration)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^{16,249} with similar findings reported for rum⁷⁰. For DMDS¹⁵³, 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 acids¹⁷⁰. The consensus is that copper distillation reduces sulphur congeners and positively influences sensory quality.

During maturation, oxidation of DMS to dimethyl-sulphoxide (DMSO) and dimethyl sulphur dioxide (DMSO₂) continues: 50% of DMS was oxidized to DMSO and DMSO₂ after 96 h in a new cask⁷⁶. 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 parameters⁷⁶ and DMTS contents decreased more slowly^{133,153}. Ratios of DMDS/DMTS form maturity indicators (30 for new-filling, 15 after 3 years¹³³). Either DMDS evaporates⁷⁶ or is converted to DMTS until concentrations fall below flavour thresholds¹³³. Sulphur compounds – particularly, thiophenes 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 thiazole¹⁵³. Addition of oak wood (chips) and air reduces sulphur congeners notably methionyl acetate and ethyl methionate¹⁷⁶.

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 butyrate²⁶ with *rancid* (*sickly*) *sour* notes at low

mashing temperatures or if wash stands in cast iron vessels¹⁸⁹. Propionic, *iso*-butyric and *iso*-valeric acids have similar characters in whisky and are abundant in rum and brandy¹⁸². In whisky *iso*-valeric acid, present in concentrations related to yeast and fermentation conditions, dominates¹⁸².

Rancio, a Cognac character reminiscent of musty walnuts, can be confused with *rancid* in whiskies. This *rancio* character, indicating an old, well-stored cognac increasing with age in parallel with *fineness* and *mellowness*²⁴. The gradually acquired *rancio* is from hydrolysis of fatty acid esters with oxidation to the ketones¹⁴⁷: 2-heptanone, 2-nonanone, 2-undecanone and 2-tridecanone. Concentrations are functions of peroxidases and cask volume²⁶⁴. Long chain aldehydes, methyl ketones (C₇, C₉ and C₁₁), glyoxal and methyl glyoxal are related to *rancio* characters in old wine-spirits (e.g. Armagnac, Cognac)^{19,264,265}. Glyoxal is present in whisky, but at concentrations too low to be quantified²¹² and *Rancio* character has not been explicitly identified. *Buttery/rancio* notes in wine¹⁵ are related to N-(3-methylthiopropyl) acetamide and 3-methylthiopropionic acid from methionol.

L. Oily characters

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

Buttery characters are related to diacetyl (2,3-butanedione), an off-note in lagers²⁵⁴. Diacetyl and 3-hydroxy butanone are also important in wines, especially sweet Sherries^{150,279}. Diacetyl is produced by citrate-metabolising lactic acid bacteria^{8,253} and in yeast fermentations formed from α -acetolactate and metabolised to acetoin. Yeast metabolism can be manipulated to produce acetoin directly from α -acetolactate²⁶⁷. In whisky nosing, diacetyl has a detection threshold of 0.02 mg litre⁻¹, a recognition of 0.04, and in tasting is 0.2 mg litre⁻¹^{127,267}. Fermentation oxygen influences spirit diacetyl content²².

T. Primary taste

T.1. *sweet*

Oak maturation influences time intensity factors (maximum intensity and duration) of sweet taste in sugar cane spirit (cachaça)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 character²⁰⁹. In whisky, congeners conferring sweet are extracted from wood largely within 3 years^{216,226}. Glycerol primarily from wood triglycerides²¹⁶ may also be generated by trans-esterification of triglycerides and ethanol, yielding fatty acid ethyl esters

and free glycerol²¹⁸. In Bourbon whiskies stave hemicelluloses and acid-catalysed hydrolysis of tannins yield monosaccharides (arabinose, glucose, xylose, galactose and rhamnose)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, proto-quercitol and arabinose are reported the most abundant in whiskies^{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 extractions¹⁸¹. 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 retailed whiskies are thought too low (Table IV) to induce *sweet*^{138,209} characters – detection threshold is approximately 5 g litre⁻¹ in water⁴. Ethanol, enhancing water structures through hydrophobic effects^{75,230}, decreased *sweetness* intensity and persistence in sugars⁹⁶. In summary it is believed that sugars make lesser contributions to flavour²⁰⁹ than other congeners such as vanillin, whisky lactone and maltol. *Fruity, woody, floral* and *buttery* characters enhances *sweet* characters in whisky²⁰⁹. However, Swan has suggested products of hemicellulose degradations add *fudgey* and *caramel* notes and colour to whisky, those of cellulose have little impact (Swan, J., unpublished).

T.2. *sour*

Wood-derived acids and esters in whiskies are thought to influence flavour little¹⁸¹. Wood-derived non-volatile congeners in matured whiskies include: oxalic, fumaric, succinic, methyl- and methoxy succinic, mesaconic, adipic, phthalic, azelaic, sebacic and trimethylbenzoic acids. New distillate has a fixed acidity of zero¹³⁴ but over 12 months the extraction of acids, oxidations of ethanol and other congeners and other reactions produce an acidic environment¹³⁴. A typical matured whisky is pH <4.5⁵⁶.

T.3. *salty*

This character, often adopted in whisky flavour evaluations, is of uncertain origin. It is possibly associated with peat bogs close to a sea, saturated with marine spray and seaweed relics¹⁴¹. Coastal warehousing with permeation by damp salty air could produce *salty* characters¹⁴¹.

T.4. *bitter*: see section M (moutheffect) – *astringent*

M. Mouth effect (*mouthfeel*)

- M.1. *warming – alcoholic, burn, fiery*
- M.2. *coating – oily, creamy feeling*

A highly intense *biting* sensation, described as *burning*, can increase to a pain sensation. *Burning* also includes a *warm* sensation¹⁰².

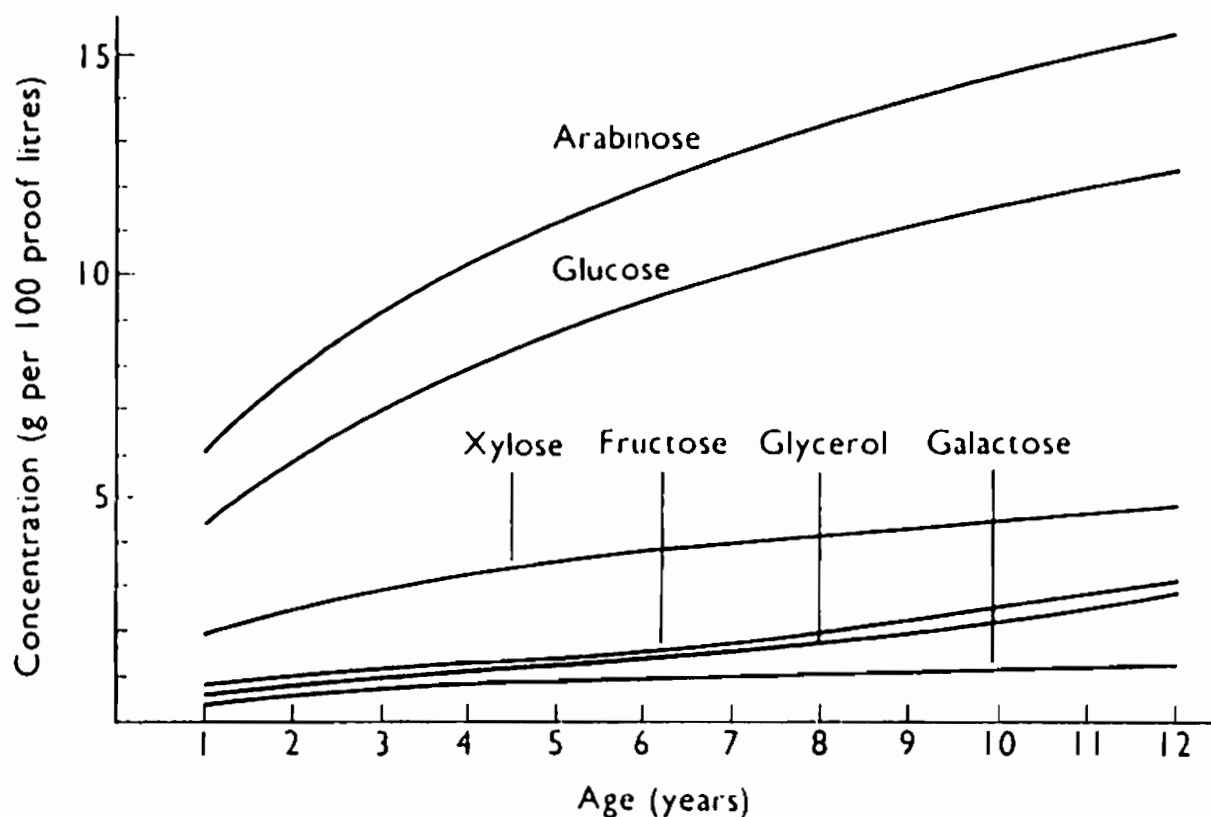


FIG. 8. Changes in sugars and glycerol during maturation (Reazin, 1981, reproduced with permission from *American Journal of Enology and Viticulture*, 32, 284).

TABLE IV. Contents (mg litre^{-1}) of sugars in some whiskies.

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

(Nykänen *et al.*, 1984; reproduced with permission from *Helsinki Foundation for Biotechnical & Industrial Fermentation Research*, 1984, 141)

In many products the term *creaminess* is important for appearance, flavour or texture⁶⁴. In whisky, understanding of the character is limited but related to mouthfeel¹⁰³ and also described as 'length in mouth'⁸¹. Perception could be related to *thickness*, *smoothness*¹¹⁵ and *fatty mouthfeel*³⁹ and is closely related to *buttery* (diacetyl) in many foods and whisky^{81,97,111,128,166}. 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* character²⁷⁹. 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-tannins^{37,177}. 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 acetal; and formation of esters from acids (e.g. acetic acid) and alcohols. Tannic substances assist char layers in removal of distillate sulphides^{35,165} and nitrogen compounds⁷⁶. Ellagitannins, abundant in raw wood, in excess confer undesirable flavour characters – contents can be reduced by hot water extractions or charring^{73,142}. Ellagitannin hydrolyses to gallic and ellagic acids, absent from new distillate¹⁶⁴ 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 maturation 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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