Whisky, Whiskey and Bourbon: Composition and Analysis of Whisky

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Sensory Assessment

Whisky has traditionally been assessed by expert blenders with many years of experience and training within the industry. An experienced blender knows what flavors of distillate a still can produce, which are desirable, and how a whisky is likely to develop during maturation. The blender's task is then to identify faults and deviations from the expected path of maturation and to select a specific maturation point at which a whisky can contribute to the blend. Blenders use a system of flavor description to assist their work, but their method of working is largely by comparison of samples with experience or a reference. Each sample is evaluated in terms of its similarity to an expected or acceptable product.

Scotch grain whiskies are light-bodied continuous still spirits, largely regarded as providing a background for a blend. Malt whiskies provide the majority of the character of a particular blend and, though the distilleries all produce slightly different whiskies, for convenience, they are divided into groups sharing common characteristics. The Highland malts, the most numerous, are further divided into first, second, and third classes. These are not intended to be quality evaluations, but are simply descriptive classes. The Lowland malts are not regarded as having a distinctive character and thus can be used in relatively large quantities in blends. There are three remaining Campbeltown distilleries and this group has, as a result, declined in importance. The Islay whiskies tend to be full-flavored and are usually heavily peated and thus have a significant impact on a blend even when used in small proportions. The Highland group contains most of the great whiskies that have established reputations as single malts and for their value in blending. A wide range of flavors is available and a skilled blender can make use of them to create a distinctive blend.

Formal methods of laboratory sensory analysis have also been used. Many companies use difference tests for quality control monitoring, and the whisky industry seems to have been one of the first to adopt the duo–trio and triangle tests for such purposes. Over recent years, there has also been an increasing interest in the assessment of whiskies by profiling or descriptive methods, largely for research into the origins and development of flavor in whiskies. Several broadly similar vocabularies of descriptive terms have been used. These vary mainly in the number of terms they include and therefore in the detail with which they attempt to describe flavor. They have often been presented in the form of a 'flavor wheel,' with varying numbers of concentric tiers, which while having no particular theoretical significance provide a framework for communication and training (Figure 1).

The Chemistry of Flavor Compounds

With the advancement in chromatographic techniques and, in particular, their coupling with mass spectrometry, the number of compounds identified from whisky has increased dramatically. Particular use is made of gas chromatography with a number of detectors for the measurement of volatile organic compounds. Nonvolatile constituents may be measured as a whole spectrophotometrically or individually by high-performance liquid chromatography. Problems arise as compounds of sensory importance may be present at very low concentrations (nanograms per gram). Major volatile congeners in a range of whiskies are shown in Table 1, and the major categories of compounds thought to be important in the development of flavor are discussed in the succeeding text.

Alcohols, Carboxylic Acids, and Esters

Aliphatic alcohols, acids, and esters are produced by the yeast (*Saccharomyces cerevisiae*) during fermentation, though ester formation may also occur during distillation and maturation. Saturated and unsaturated chains are found, ranging from 1 to 16 carbon atoms. Short-chain alcohols such as propanols, butanols, and pentanols are the most abundant. Nonaliphatic alcohols include 2-phenylethanol and 2,3-butanediol. The principal organic acid is acetic acid, accounting for between 50% and 90% of the total content of volatile acids. Octanoic, decanoic, and dodecanoic acids are quantitatively important, though lower-molecular-weight acids such as butanoic and pentanoic acids may have more sensory impact. The most abundant esters are the ethyl esters of the acids named, their concentrations reflecting the relative abundance of the acid. Any other combination of the acids and alcohols present may occur. After ethyl esters, the most abundant are acetate esters such as isoamyl acetate and phenylethyl acetate. The esters of hydroxy acids, such as lactic acid, and of dicarboxylic acids, such as succinic acid, can be distilled along with alcohol and steam and so occur in whisky.

Aliphatic Carbonyl Compounds

The majority of carbonyl compounds are produced by the metabolic actions of the yeast during the fermentation. However, their formation by oxidation of unsaturated fatty acids or Strecker degradations has been shown to occur at almost any stage of production. Acetaldehyde is the most common and is often used to determine total aldehydic content. Many other aldehydes, ketones, and acetals have also been identified. For aldehydes and ketones, aliphatic chain lengths, both saturated and unsaturated, range from 2 to 14 carbon atoms. Due to the high alcoholic strengths of the distillate, aldehydes exist in equilibrium with the corresponding acetal and hemiacetal. The most frequently reported acetal is 1,1-diethoxyethane, though a range of aldehydes up to six carbon atoms have been shown to form acetals.

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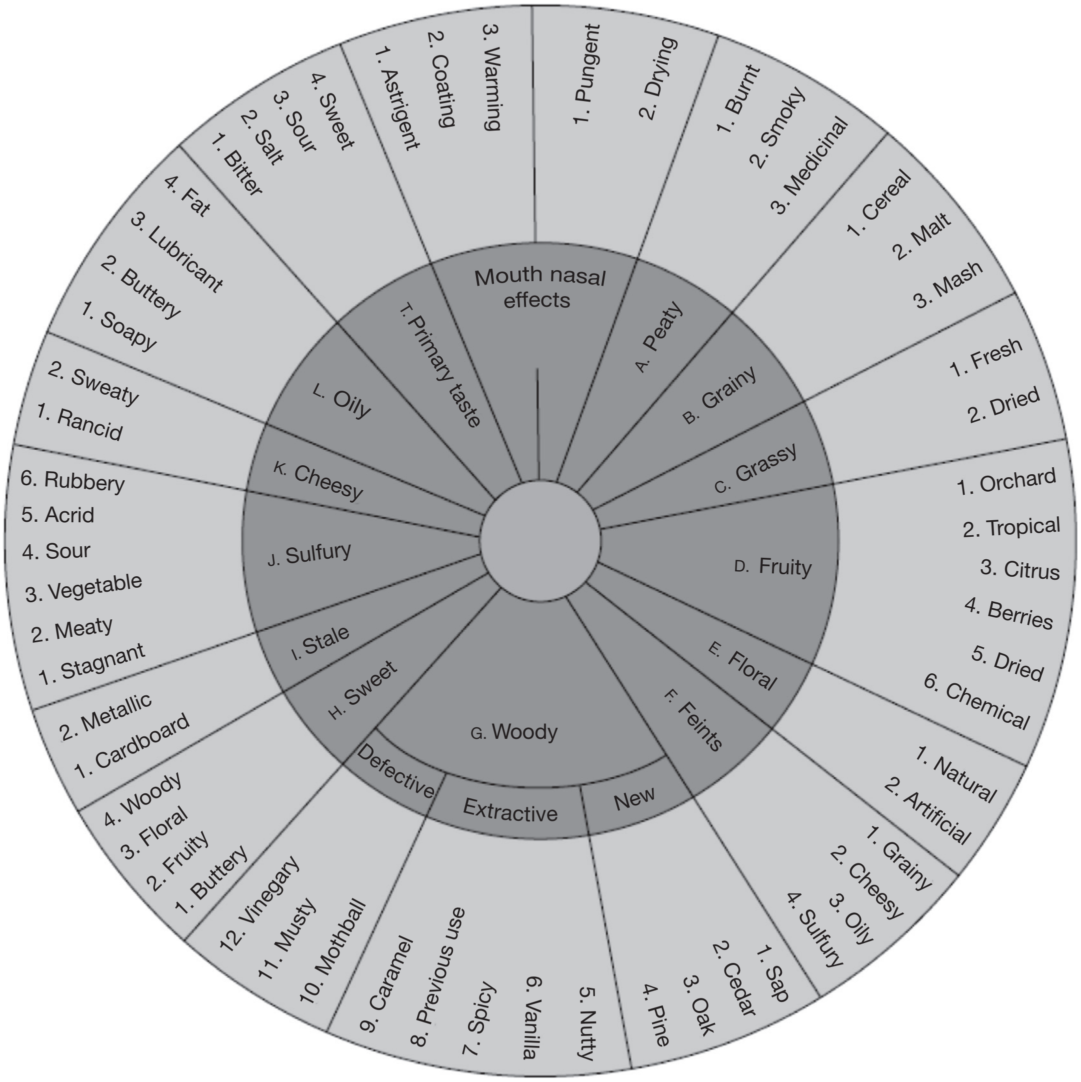

Figure 1 Whisky flavor wheel. *Note*: 'Feints,' also tails or after shots, is the final fraction of distillate, redistilled with the next batch of low wines. Reproduced with permission from Lee, K. Y. M., Paterson, A., Piggott, J. R. and Richardson, G. D. (2001). Origins of flavour in whiskies and a revised flavour wheel: a review. *The Journal of the Institute of Brewing* **107**, 287–313. Copyright 2001 The Institute of Brewing & Distilling.

Table 1 Major volatile congener concentrations (g/100 l abs. alc.) in single samples of whiskies

Whisky type	*Acetaldehyde*	*Methanol*	*Ethyl acetate*	n-*Propanol*	*Isobutanol*	*2-Methylbutanol*	*3-Methylbutanol*	*2- and 3-Methylbutanol*	*Ratio 1*	*Ratio 2*
Scotch malt whisky	17	6.3	45	41	80	62	114	176	2.2	2.8
Scotch grain whisky	12	8.5	18	72	68	8	15	23	0.3	2.8
Scotch blended whisky	5.4	8.9	23	55	62	26	46	72	1.2	2.8
Irish whiskey	4.1	10	13	28	15	18	32	49	3.1	2.8
Kentucky bourbon whiskey	15	17	89	28	160	143	242	385	2.4	2.7
Canadian whisky	3.3	7.9	7.1	6.2	6.9	7	9	16	2.3	2.2

Ratio R1 = 2- and 3-methyl butanol/isobutanol; ratio R2 = 3-methylbutanol/2-methylbutanol.

Source: Reprinted from *Whisky technology, production and marketing*. Aylott, R., Whisky analysis, pp. 275–306. Copyright (2003), with permission from Elsevier.

Table 2 Concentrations (micrograms per liter at 100% alcohol) of sulfur compounds in malt whiskies of various ages

Compounds	*Age (years)*				
	0	*1*	*2*	*3–5*	*6–10*
Dimethyl disulfide	359	345	272	149	91
Dimethyl trisulfide	12	16	15	19	14
3-(Methylthio)propanal	7	t	0	0	0
Dihydro-2-methyl-3(2H)-thiophenone	77	53	3	0	0
Ethyl 3-(methylthio)propionate	21	11	t	0	0
3-(Methylthio)propyl acetate	274	139	3	0	0
2-Thiophenecarboxaldehyde	66	83	49	60	54
3-(Methylthio)propanal	8	0	0	0	0
5-Methyl-2-thiophenecarboxaldehyde	15	15	10	16	16
Benzothiophene	39	27	27	31	38
Benzothiazole	18	16	14	15	32

t, trace.

Source: Masuda, M. and Nishimura, K. (1981). Changes in volatile sulfur compounds of whisky during aging. *Journal of Food Science* **47**, 101–105. Copyright © 2006, with permission from John Wiley and Sons.

Sulfur and Nitrogen Compounds

Yeasts have the ability to utilize inorganic sulfur, sulfur-containing amino acids and vitamins, and from these sources, volatile sulfur-containing compounds are produced. The range of compounds detected include heterocycles, such as thiazoles and thiophenes, and aliphatic mono-, di-, and trisulfides. The formation of sulfur compounds has also been shown to occur during distillation and concentrations are highest in new spirit. Cask char, wood extractives, and traces of elemental copper are important in the degradation of such compounds during maturation (Table 2). Heterocyclic nitrogen compounds such as pyrazines, pyrroles, and pyridines are formed via the Maillard reaction during cooking, mashing, distillation, and barrel charring. As they have relatively low odor thresholds, they may well make a contribution to the aroma of whisky.

Phenols

A wide range of phenolic compounds are found in whisky. Simple phenols such as phenol, the isomeric cresols, xylenols, ethyl phenols, and guaiacols arise through the thermal degradation of benzoic acid derivatives from malt and from peat smoke. Phenolic aldehydes such as vanillin, syringaldehyde, coniferaldehyde, and sinapaldehyde are formed from the breakdown of wood lignin during cask charring and maturation. Their corresponding acids and ethyl esters have also been detected. Polyphenols extracted from the wood include ethanol-soluble lignin and tannins derived from both gallic and ellagic acids.

Heterocyclic Oxygen Compounds

The main types of these compounds found in whisky are furaldehydes and lactones. Furfural (2-furaldehyde) is formed from pentoses and 5-hydroxymethyl-2-furaldehyde from hexoses via the Maillard reaction during mashing, distillation, and cask charring. Lactones are formed by the dehydration of aliphatic hydroxy acids and most are derivatives of 2(3H)-furanones. The most abundant of these are the cis and trans isomers of 5-butyl-4-methyldihydro-2(3H)-furanone, the oak or whisky lactones, which are formed and extracted from oak casks during maturation.

Variations with Processing

Though there are only four basic processes in whisky production, local, regional, and national variations in these processes are responsible for the large number of whiskies available. Each stage of production, from the production of a fermentable extract, to fermentation, to distillation, to maturation, can affect the character of the final product. However, each stage is interlinked and identifying one, as the most important for a particular type of whisky, is often impossible.

The Production of a Fermentable Extract

The cereal grains in common use are wheat, corn (maize), rye, and barley, though the choice of cereal is often legally restricted. Flavor differences between cereals arise from two quite separate sources: the composition of the extract and the levels of precursors present. The choice of cereal can also indirectly affect the flavor of the final product. The composition of the fermentable extract varies with cereal used and can influence the metabolism of the yeast. Factors such as pH, amino acid concentration, and levels of insoluble material are known to affect the levels of fusel alcohols, acids, and esters produced, which may influence the flavor of the final product. Between cereals, differences also exist in the levels of precursors for a number of classes of flavor compounds. Examples are compounds formed by the chemical and enzymatic oxidation of fatty acids, the reaction of free amino acids and reducing sugars (Maillard reaction), and the thermal degradation of biosynthesized precursors like *S*-methylmethionine and benzoic acid derivatives. However, the breakdown of these compounds frequently occurs during fermentation and distillation and is affected by variations in these processes. Consequently, no flavors in the final product have been unequivocally linked to components of the original cereal.

Fermentation

Fermentation is responsible for the primary production of a large number of flavor compounds in whiskies. Factors that are known to alter the production of these compounds are the strain or mix of yeasts used, design and level of aeration in the fermenter, the duration of the fermentation, and the presence of contaminating bacteria. These factors alter according to distillery design and the raw materials employed and so may be important in producing regional and national differences in whiskies.

Distillation

In batch distillation using pot stills, the selection of the cut points in the still run has a marked influence on the flavor of the product. Generally, aldehyde and short-chain ester concentrations are determined by the primary cut from foreshots to spirit, while the concentration of fusel alcohols and acids is determined by the cut from spirit to feints. Other factors, which affect the physical process of separation during distillation, are still design parameters such as the still height, the angle, and length of the lyne arm and the type of condenser used. In addition, a number of chemical reactions can occur when the wash or low wines are heated for distillation. This is particularly true for batch distillation in pot stills where the heat impact is greater. Examples include the formation of sulfur compounds from sulfur-containing amino acids, the breakdown of unsaturated fatty acids to carbonyl compounds, and the dehydration of β-hydroxypropionaldehyde to acrolein. Copper catalyzes many of these reactions.

In continuous stills, congener concentrations are determined by the design, operation, and efficiency of the still. The range of reactions described for pot stills can still occur but become progressively less important as distillate strength increases. Collection of spirit at high ethanol concentrations (>90%) results in low levels of congeners in the spirit.

Maturation

During the maturation period, the new distillate becomes highly modified as a result of its contact with the cask (Figure 2). The composition of the cask wood has a major effect on the extent of this modification and varies with the species of oak used, the pretreatment applied to the wood, and the previous use of the cask. In general, American oak (*Quercus alba*) yields higher concentrations of vanillin and *cis* oak lactone, while Spanish oak (*Quercus robur*) gives higher concentrations of tannins. Charring increases the levels of lignin breakdown products and lactones extracted during maturation, whereas previous use of a cask greatly reduces the amount of extractable lignin breakdown products and lactones. The use of sherry casks results in raised levels of tannins and sugars. The cask is the major determinant of mature quality, but other factors such as filling proof, climate, and warehouse conditions also affect the course of maturation. Higher temperatures produce greater evaporation rates and also increase extract levels and some reaction rates, but do not necessarily produce a more mature product.

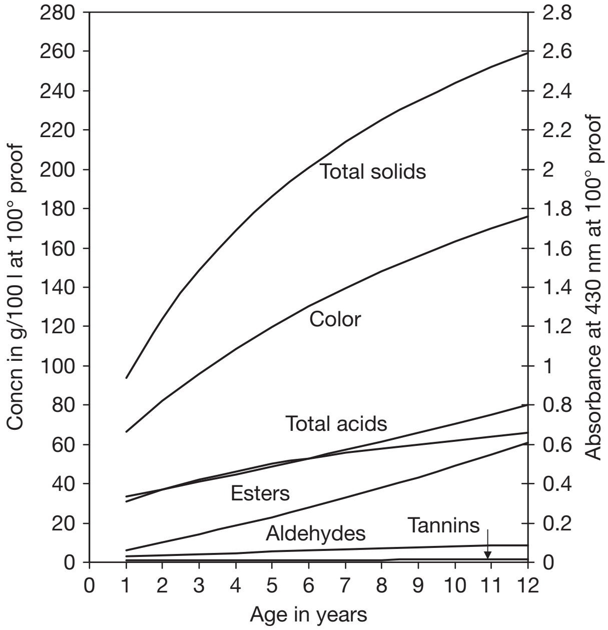

Figure 2 Congener changes during maturation of whisky. Reprinted from Baldwin, S. and Andreasen, A. A. (1974). Congener development in Bourbon whisky matured at various proofs for twelve years. *Journal of the AOAC* **57**, 940–950. Copyright 1974 by AOAC INTERNATIONAL. Permission is granted for a reprint of Figure 8.

Correlation of Chemical Composition with Sensory Data

The flavor of whisky is dependent upon a complex mixture of components that originate from and are modified by different stages of production. While improved analytical methods have revealed much about the chemistry of whisky, this has not resulted in a better understanding of the chemical basis of whisky flavor and quality. Frequently, chemical differences can be related to variation in production processes, but identifying the actual compounds responsible for the flavor differences has been much more elusive.

The extent to which volatile compounds from cereals survive fermentation, distillation, and maturation is the hardest to establish. Whisky prepared from heavily peated malt retains a characteristic medicinal, smoky flavor that is strongly correlated with the total phenols content of the malt and of the whisky. However, the range and concentration of phenols present are greatly altered by mashing, fermentation, and distillation and whether the phenols fully explain the 'peated' flavor is still uncertain. Likewise, some whiskies (especially Canadian) have a characteristic 'spicy' or 'minty' flavor, which is possibly related to the use of rye in the mash, but no compound has been identified as responsible.

Various flavors in new distillates have been correlated with sulfur compounds. Polysulfides are present in whisky at levels around and above their sensory thresholds (3–6 ng g^{-1} for dimethyl trisulfide), and the data available suggest that these compounds are correlated with 'sulfury' and 'heavy' characters in fresh distillates. Other sulfur-containing compounds are thought to be important contributors to flavor, and their formation is dependent on the levels of precursors present in different cereals/cultivars. However, such compounds are frequently formed during fermentation and distillation and then degraded during maturation. Each stage has its own impact on the concentration in the final product making it harder to establish their role in whisky flavor.

The products of fermentation and distillation make a substantial contribution to whisky flavor. However, these compounds, except when present in excess, appear to form what has been described as the 'integrated whisky complex,' and their individual contributions have not been determined. It does appear that relatively constant proportions of some of these compounds must be present for a recognizable 'whisky' character, though substantial changes can occur with only minor changes in flavor.

Compounds considered to be important in maturation are vanillin, eugenol, and *cis* oak lactone. These have been correlated to 'vanilla' and 'clove-like' flavors in some whiskies matured in new casks. However, cask reuse causes a general decrease in wood extractives and their importance in whisky matured in refill casks is still uncertain.

Attempts to create a model of whisky flavor have been largely unsuccessful. Attempts were based on compositional analyses of the liquid. Research has since shown that there are complex relationships governing the release of flavor compounds from whiskies. Major factors identified include alcoholic strength and the nonvolatile content of the whisky matrix. Dilution of spirits for sensory assessment, to reduce the pungency of ethanol, can greatly alter the release of aroma compounds more soluble in ethanol than in water. Dilution also increases the capacity for matrix effects that suppress the release of ethyl esters and other aroma compounds. Matrix effects may occur through competition for release at the liquid surface or changes in solubility of flavor components. Changes in solubility can be related to the physical structuring of the ethanol–water mixture. Differential scanning calorimetry, light scattering, and mass spectrometry have all demonstrated that physical changes occur during maturation, adding another layer of complexity to whisky flavor and reinforcing the uniqueness of each individual product.

Health Effects

Apart from the well-known benefits of light to moderate alcohol consumption, whisky, in common with some wines and other wood-matured spirits, contains phytochemicals with potentially beneficial effects. Most attention has been given to antioxidants, but wood and spirit matured in it contain a range of other components with possible effects, such as amelioration of allergic reactions. Phytophenols may also reduce the rate of alcohol metabolism, thereby reducing blood acetaldehyde level and prolonging exposure to alcohol. In animal models, whisky has also been found to have a less damaging effect on the stomach compared with aqueous ethanol. The highest antioxidant activity has been found in red wines, followed by Armagnac, Cognac, whiskies, and some wood-aged rums, with white spirits showing no activity. The extent of the activity varies with the maturation time, older spirits showing greater activity, and with the wood and its heat treatment before use. Oak, the species used most commonly for spirit maturation, is among the most active. Activity is correlated with the total phenolic content and with ellagic acid, a major component of the wood-derived materials present in matured spirits. In some studies, flavonoids have been found to be most important for the antioxidative capacity of spirits, whereas in other cases, nonflavonoids appear to be important. Consumption of alcoholic beverages containing phenolic compounds transiently raises plasma phenol concentrations and antioxidant capacity in humans, but as yet, there is little evidence of any real benefit in terms of chronic disease risk.

See also: Antioxidants: Role on Health and Prevention; Browning: Non-enzymatic browning; Chromatography: Focus on Multidimensional GC; Chromatography: Combined Chromatography and Mass Spectrometry; Chromatography: High-Performance Liquid Chromatography; Mass Spectrometry: Principles and Instrumentation; Mass Spectrometry: Applications; Phenolic Compounds: Occurrence, Classes, and Analysis; Sensory Evaluation: Sensory Rating and Scoring Methods.

Further Reading

Bryce JH and Stewart GG (eds.) (2004) *Distilled spirits: tradition and innovation*. Nottingham: Nottingham University Press.

Bryce JH, Piggott JR, and Stewart GG (eds.) (2008) *Distilled spirits: production, technology and innovation*. Nottingham: Nottingham University Press.

Di Castelnuovo A, Costanzo S, Bagnardi V, Donati MB, Iacoviello L, and de Gaetano G (2006) Alcohol dosing and total mortality in men and women – an updated meta-analysis of 34 prospective studies. *Archives of Internal Medicine* 166: 2437–2445.

Duthie GG, Pedersen MW, Gardner PT, Morrice PC, Jenkinson AM, McPhail DB, and Steele GM (1998) The effect of whisky and wine consumption on total phenol content and antioxidant capacity of plasma from healthy volunteers. *European Journal of Clinical Nutrition* 52: 733–736.

Jacques KA, Lyons TP, and Kelsall DR (eds.) (2003) *The alcohol textbook*, 4th ed. Nottingham: Nottingham University Press.

Kilcast D (ed.) (2010) *Sensory analysis for food and beverage quality control: a practical guide*. Cambridge: Woodhead Publishing.

Lee KYM, Paterson A, Piggott JR, and Richardson GD (2001) Origins of flavour in whiskies and a revised flavour wheel: a review. *Journal of the Institute of Brewing* 107: 287–313.

Piggott JR (ed.) (2011) *Alcoholic beverages: sensory evaluation and consumer research*. Cambridge: Woodhead Publishing.

Piggott JR, Sharp R, and Duncan REB (eds.) (1989) *The science and technology of whiskies*. Harlow: Longman.

Russell I (ed.) (2003) *Whisky: technology, production and marketing*. London: Academic Press.

Van der Gaag MS, van den Berg R, van den Berg H, Schaafsma G, and Hendriks HFJ (2000) Moderate consumption of beer, red wine and spirits has counteracting effects on plasma antioxidants in middle-aged men. *European Journal of Clinical Nutrition* 54: 586–591.

Walker GM and Hughes PS (eds.) (2010) *Distilled spirits: new horizons: energy, environmental and enlightenment*. Nottingham: Nottingham University Press.

Walker GM, Goodall I, Fotheringham R, and Murray D (eds.) (2012) *Distilled spirits: science and sustainability*. Nottingham: Nottingham University Press.