V The Development of Flavour in Potable Spirits

By J. S. Swan and S. M. Burtles
PENTLANDS SCOTCH WHISKY RESEARCH LTD.,
84 SLATEFORD ROAD, EDINBURGH E11 1QU

1 Introduction

Potable spirits are distinct from most other food products in so far as they are homogenous solutions, thus presenting a medium for flavour studies which is free from the problem of flavour release due to the intricacies of texture. Even the study of aroma in carbonated beverages may be influenced by the effect of CO_2 release. However in common with most other products the number of components present is large and their low concentrations render accurate analyses very difficult.

Kahn[54] reported in 1969 that 226 compounds had been observed in whisky and since then at least another 30 have been reported. In the case of beverages matured in wood, *e.g.* whisky, brandy, and rum, the total level of flavour components rarely exceeds 1 % of the total weight (and is normally very much lower) in a base of 40—45 % ethyl alcohol. This high concentration of ethyl alcohol presents particular problems in both sensory and analytical studies. Furthermore the many analytical studies reported since the advent of gas chromatography show that most potable spirits contain the same components. It follows therefore that the nuances of flavour are essentially attributable to small differences in the relative proportions of these components.

In 1966, Guadagini and co-workers made an important contribution to the interpretation of flavour in food products by the introduction of the term odour unit[55] where:

Odour Unit (Ou) = concentration present/threshold concentration.

Further, if the sum of the odour units from each fraction in a mixture equals, or nearly equals the whole, then the contributions of the individual fractions may be considered additive and each contribution may be expressed as a percentage: 100 × Ou fraction/Ou whole = % odour contribution from each fraction. If the sum of the fractions is substantially less or greater than the whole the presence of suppressive or synergistic effects may be postulated.[56]

Using this type of approach Salo, Nykanen, and Suomalainen[57] studied the odour thresholds and relative intensities of volatile aroma components in an artificial beverage imitating whisky. The beverage contained 67 ingredients

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[54] J. H. Kahn, JAOAC, 1969, **52**, (6), 1168.

[55] D. G. Guadagni, R. G. Buttery, and J. Harris, *J. Sci. Food Agric.*, 1966, **17**, 142.

[56] P. Salo, Proceedings International Symposium Aroma Research, Zeist, Pudoc Wageningen, 1975, 121.

[57] P. Salo, L. Nykanen, and H. Suomalainen, *J. Food Sci.*, 1972, **37**, 394.

consisting of acids, alcohols, esters, and carbonyl compounds. From a knowledge of the concentrations and odour thresholds of all the substances present they determined that the alcohol group contributed 4% of the total aroma, the acids contributed 3.5%, the esters 26%, and the carbonyl group 58% (Figure 6).

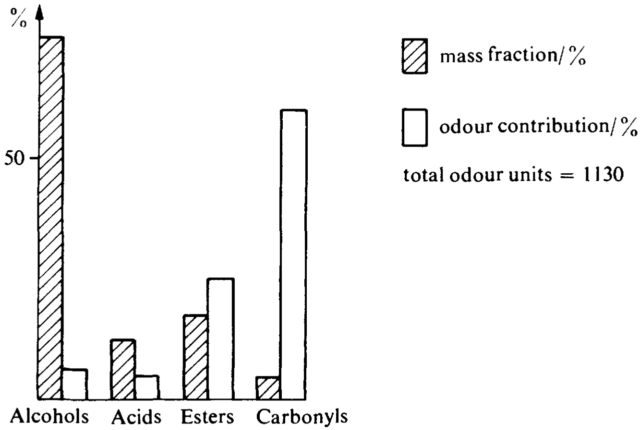

Figure 6 *Mass fraction % of alcohols, acids, esters, and carbonyl compounds and their contributions to odour units of a whisky imitation*[56]

Normally the components present in this artificial beverage derive from the fermentation stage of the process as a result of the action of yeast upon the sugar containing substrate. Whilst the choice of yeast strain and the fermentation conditions undoubtedly influence the composition of the volatiles produced[58] and control of these features are of vital importance in the brewing industry, such precise control is of lesser importance in potable spirits production owing to the modifying influence of the distillation, maturation, and blending stages which follow. Traditionally at least, potable spirits with characteristic and reproducible flavour have been produced with little deliberate control of fermentation conditions. In potable spirit production it is desirable to produce the maximum yield of alcohol and consequently the wort is not sterilized prior to fermentation, in order to preserve enzyme activity, thus permitting the production of volatile compounds from competing bacterial fermentations.

Whilst the production of flavour volatiles during yeast fermentation has been extensively studied, less attention has been given to those other aspects of the process and their overall contribution to flavour. It is proposed to do so here, and it is suggested that the odour construction of the artificial whisky might be used as a model for assessing the nuances of flavour between different spirits brought about by the influence of other stages of the process in contributing additional classes of compounds or their modifying role upon the relative proportions.

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[58] H. Suomalainen and M. Lehtonen, *Kemia Kemi*, 1976, **2**, 69.

Scheme 3 shows the production process for the manufacture of Scotch whisky and with certain modifications it may be used for other whiskies as well as rum and brandy. Thus, whisky in some countries is produced without the malting process by the action of enzyme products on the cereals, whereas if the malting and mashing stages are replaced by the crushing of grapes or the dilution of molasses the scheme suitably represents brandy or rum production.

Malting ↓	Enzymatic conversion of starch to fermentable sugars
Mashing ↓	Solubilization of the fermentable sugars
Fermentation ↓	Production of alcohol and secondary products by the action of yeast
Distillation ↓	Fractionation in continuous (equilibrium) stills or in pot (batch) stills. Always in copper
Maturation	Flavour modification in oak wood

Scheme for the production of Scotch whisky

Scheme 3

Examples of other classes of compounds which may contribute to aroma are the phenols, organonitrogen compounds, and organosulphur compounds. In practice the reason for scarcity of knowledge of their role in spirit flavour is of course due to the difficulties of accurate analysis and of obtaining pure samples for sensory studies.

2 Production and Influence of Volatile Phenols

As long ago as 1895 Zwaardemaker[59] listed phenol as an example of an empyreumatic or burned aromatic. For even longer, Scotch malt whiskies have been identified as possessing smokey aromas and this has been attributed to the traditional process of drying the malt over peat smoke.[60] Whilst the measurement of adsorbed phenols is taken as an indication of the degree of peating, Deki and Yoshimura[61] identified some 80 aroma components in peated malt. Bathgate and Taylor[62] recently grouped these into three major divisions namely: (*a*), hydrocarbons; (*b*), furfurals; (*c*), phenols; and pointed out that it is still not certain that the phenolic constituents are the major contributors to the characteristic smokey aroma. Studies on the analysis of phenols in peated malt samples and the odour potency of phenols in whisky[63] indicate that these compounds could

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[59] H. Zwaardemaker, 'Die Physiologie des Geruchs', Engelmann, Leipzig, 1895.

[60] J. A. Nettleton, in 'The Manufacture of Whisky and Plain Spirit', Cornwall and Sons, Aberdeen, 1913, p. 308, 310, 319.

[61] M. Deki and M. Yoshimura, *Chem. Pharm. Bull.*, 1974, **22,** 1748, 1754, 1760.

[62] G. N. Bathgate and A. G. Taylor, *J. Inst. Brew*, 1977, **83,** 163.

[63] J. S. Swan, S. M. Burtles, and D. Howie, in preparation.

provide a significant contribution to the aroma of the spirit. Table 13 shows the analysis of the major phenols present in a peated malt sample along with the odour units which could result in the spirit produced, assuming an average distillery yield. These studies also indicate that the odour potency of such phenols is approximately doubled when combined into a group of this nature, thus providing a potential of 81 odour units. When compared to the total odour units in the artificial model[57] this represents a contribution of around 7% derived entirely from the peating of the malt. It is probable however that owing to the contribution of the hydrocarbon and furfural groups, whatever the magnitude, that a true peated aroma can only be obtained at present by the conventional process of kilning.

Table 13 *Phenol fraction in a typical peated malt and possible impact in malt whisky*

Phenol	*Conc. in malt* mg/kg^{-1}	*Potential conc. in spirit* p.p.m. at 40% alc.	*Odour threshold* p.p.m.*	*Odour units*
Phenol	3.1	3.3	40	0.08
o-Cresol	0.25	0.26	0.3	0.9
m + *p*-Cresol	0.60	0.64	0.06	10.6
p-Ethyl phenol	0.22	0.23	0.6	0.38
2, 3-Xylenol	0.06	0.06	0.5	0.12
p-Ethyl guaiacol	0.03	0.03	0.05	0.6
Eugenol	1.32	1.40	0.05	28.0
			Total	40.68†

*determined in 20% ethanol–water base using the ascending series method
†when adjusted for observed synergism the total becomes 40.68 × 2 = 81.36 units

Phenols have also been detected in rum[64,65] and other types of whisky[66,67] and it appears that they can be produced during the mashing, fermentation, and maturation stages. In the late 1950s Whiting and Carr[68,69] demonstrated that volatile phenols could be produced by the action of *Lactobacillus pastorianus* on phenolic acids which are present in many natural products. Steinke and Paulson[70] in 1964 demonstrated that *p*-vinyl phenol and *p*-vinyl guaiacol are formed by thermal decarboxylation during mashing, and microbiological decarboxylation during fermentation, from *p*-coumaric and ferulic acids. Subsequent yeast and bacterial action converts these intermediates into *p*-ethyl phenol and *p*-ethyl

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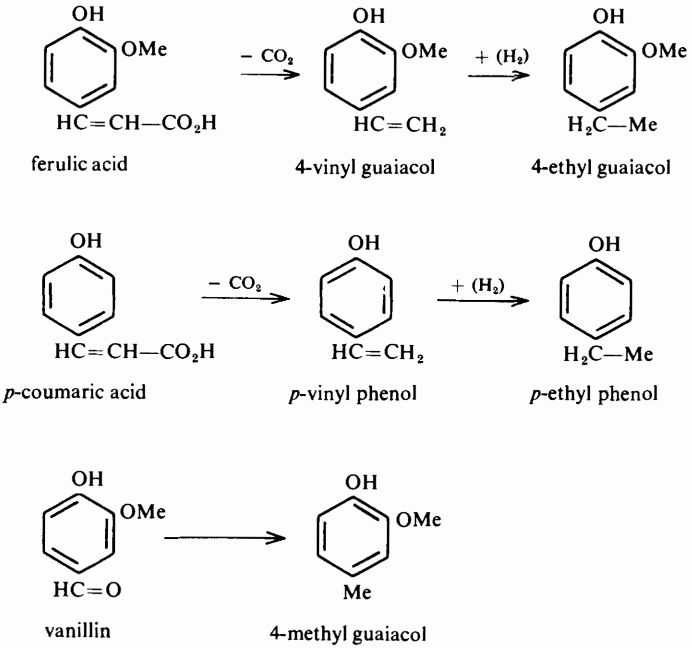
[64] P. Dubois, G. Brule, and J. Dekimpe, *Industr. Aliment. Agric.*, 1972, **89**, no. 1, p. 7.
[65] P. Dubois and J. Rigaud, *Ann. Technol. Agric.*, 1975, **24**, no. 3—4, p. 307.
[66] K. Nishimura and M. Masuda, *J. Food Sci.*, 1971, **36**, 819.
[67] J. H. Kahn, P. A. Shipley, E. G. La Roe, and H. A. Conner, *J. Food Sci.*, 1969, **34**, 587.
[68] G. C. Whiting, and J. G. Carr, *Nature*, 1957, **180**, 1479.
[69] G. C. Whiting, and J. G. Carr, *Nature*, 1959, **184**, 1427.
[70] R. D. Steinke and M. C. Paulson, *J. Agr. Food Chem.*, 1964, **12**, no. 4, p. 381.

guaiacol, and *p*-methyl guaiacol may be similarly produced from vanillin (Scheme 4).



Transformation of precursors to steam volatile phenols[70]

Scheme 4

Volatile phenols also appear to be produced during maturation by the action of ethanol on oak. Soumalainen[58] and co-workers demonstrated that guaiacol, phenol, *m*-cresol, vanillin, and particularly eugenol can be formed in this way. It may be concluded that the presence of volatile phenols in potable spirits is largely attributable to the breakdown of naturally occurring phenolic acids deriving from a variety of sources, *e.g.* peat, corn, and oakwood.

3 α and β Ionone

The ionones have intense violet-like aromas and a threshold of 7 × 10^{-6} p.p.m. (0.007 p.p.b.) for β-ionone in water has been reported.[71] La Roe and Shipley[72] have detected the presence of these compounds in American, Canadian, Scotch, and Irish whiskies as well as grape brandy. They showed that these compounds can result from the thermal decomposition of β-carotene in grain under the conditions prevailing during the mashing or cooking process. It may therefore

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[71] R. G. Buttery, R. M. Seifert, D. G. Guadagni, and L. C. Ling, *J. Agr. Food Chem.*, 1971, **(19)** **3**, 524.

[72] E. G. La Roe and P. A. Shipley, *J. Agr. Food Chem.*, 1970, **18**, 174.

be anticipated that small variations in operating conditions between distilleries may result in the production of varying quantities of these components.

4 The Influence of Distillation on Congener Composition

Distillation of potable spirits may take place in either continuous, multiplate fractionating columns, or in simple pot stills by two or three successive distillations. In continuous stills the system operates under equilibrium conditions and has been extensively studied elsewhere, particularly in the petrochemical industry. The degree of sophistication of continuous stills in use varies widely fom the two column Coffey-type still most commonly used in Scotch grain whisky production (Figure 7) to more elaborate 2, 3, or even 4 column units which provide more fractionation and improved extraction of feints.

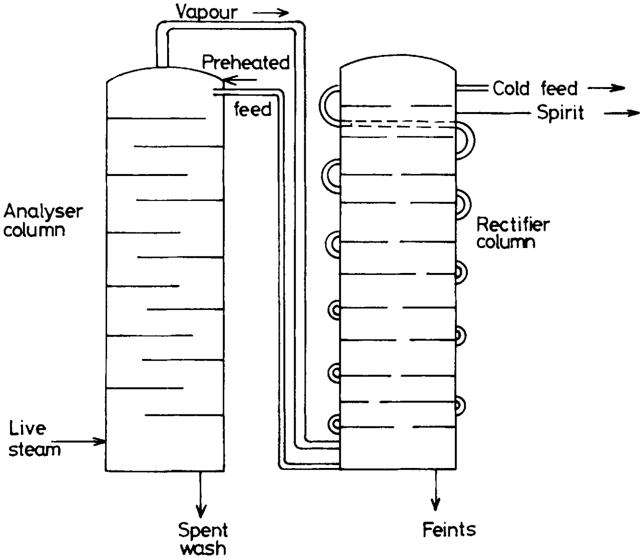

Figure 7 *Coffey still used for Scotch grain whisky distillation*

Reviews of continuous still distillation of Scotch grain whisky[73] and Californian brandy[74] show that the various flavour components distribute themselves fairly sharply around particular plates in the column according to their boiling point. Accordingly the level of components in the spirit produced depends upon the choice of plate (*i.e.* spirit strength) at which the spirit is removed. In Scotch grain whisky production the product is drawn off at ~ 94% alcoholic strength and is therefore much 'lighter' than Californian brandy ~ 84% (maximum).

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[73] M. Pyke, *J. Inst. Brewing*, 1965, **71**, 209.

[74] J. F. Guymon, in 'Chemistry of Winemaking', ed. A. Dinsmoor Webb, American Chemical Society, Washington, 1974.

By contrast pot still distillation is a batch process where equilibrium conditions are not achieved and mathematical treatments are more complex. Generally speaking however, spirits produced by this procedure, *e.g.* pot still distillation of malt whiskies in Scotland, Cognac brandy produced by the 'Methode Charentaise' and the 'Heavy Continental' rums are preferred by connoisseurs and enjoy a price advantage over continuous still products, and it must be observed that the relative proportions of flavour components is different with pot still distillates compared to continuous still distillates even when drawn at the same strength.

Pot stills are always constructed in copper, are rarely lagged, and the reflux area of the neck is usually void. A diagram of a typical Scotch whisky still is shown in Figure 8. Consequently the heat input substantially exceeds the actual heat required to volatilize the fermented liquors and the degree of fractionation approximates to a single theoretical distillation stage. In terms of flavour the pot still may be regarded as a reaction vessel and the following examples can be cited to illustrate the point.

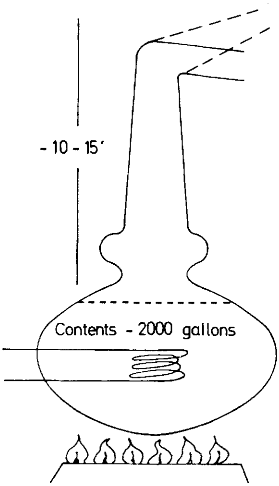

Figure 8 *Typical traditional Scotch malt whisky still. Either direct heating by gas or coal or indirect heating by steam coils may be used*

(1) Recently Nemoto[75] in a study of rum-making utilizing butyric acid bacteria reported substantial increases in the levels of ethyl acetate and ethyl butyrate during distillation of the corresponding acids in 10% ethanol solution. They also determined that the extent of ester formation was very pH dependent. (Table 14).

(2) During fermentation the long chain esters of ethanol and monocarboxylic acids, *i.e.* ethyl decanoate (caprate) to ethyl hexadecanoate (palmitate) are

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[75] S. Nemoto, *Ann. Technol. Agric.*, 1975, **24**, no. 3—4, p. 397.

Table 14 *Production of esters during the distillation of organic acids in 10% ethanol solution*

Solution to be distilled			*Distillate*	
	Concentration mg/100 ml	*pH*	*Ester* mg/100 ml	*Acid* mg/100 ml
Acetic acid	106.2	2.0	6.2	48
		3.5	4.4	43.2
		5.0	0.9	48.6
	204.2	2.0	15.8	93
		3.5	4.4	88.8
		5.0	2.6	52.8
	301.1	2.0	23.8	131.4
		3.5	5.3	131.4
		5.0	5.3	87.6
Butyric acid	96.8	2.0	5.8	165.4
		3.5	2.3	157.5
		5.0	1.1	94.2
	201.0	2.0	17.4	287
		3.5	5.8	308
		5.0	5.8	178
	302.4	2.0	18.6	442
		3.5	9.3	451
		5.0	8.1	278

bound to the yeast cell wall[76] and consequently are absent from non-distilled beverages (*e.g.* beer) after separation from the yeast During distillation in pot stills however it is normal practice to charge the dead yeast cells into the stills whereupon the fatty esters are liberated and pass into the distillate. The low odour thresholds of ethyl caprate and laurate[57] enable them to make a significant contribution to the odour of the distillate whilst the longer chain esters contribute to the mouthfeel effects. These compounds are however the major contributors to chill haze and current commercial pressure requires that a proportion of these are removed by cold filtration prior to bottling.

(3) When a typical fermented liquor for whisky making is distilled in glass, the product has a strong sulphur aroma normally absent in the commercial product. Traditional distillers claim that the presence of copper is necessary to 'fix' organosulphur compounds. Studies in our laboratories[77] have shown that dimethyl sulphide in the distillate from a single stage distillation in a copper pot still is reduced by 70% compared to all-glass distillation. This explains why DMS (which has a reported threshold of 0.0003 p.p.m.[18] in water) is less troublesome in spirits production compared to ale or lager production.

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[76] K. Nordstrom, *J. Inst. Brewing*, 1964, **70**, 233.

[77] J. S. Swan and L. Hill, unpublished work.

During the distillation period of the pot still only a narrow fraction of distillate is collected as spirit ('coeur' in cognac production) and the composition of flavour components present obviously depends upon the choice of fraction. Williams[78] prepared vapour–liquid equilibrium data for many of the components in spirit distillate and Guymon[74] presented volatility curves for alcohols and esters from these data. The optimum distillation conditions for each component can therefore be calculated. It is however, traditional practice to recycle that part of the distillate which contains alcohol other than the spirit fraction. Those flavour components which are rejected initially by the choice of cut eventually must pass to the spirit fraction thus reducing the apparent influence of the physico-chemical data in predicting the composition of the final product.

5 The Influence of the Maturation Stage

The maturation stage may last from one to fifty years depending upon the type of spirit concerned. In whisky production four years to twelve years are usually allowed depending upon the type and quality of the products. Maturation always takes place in oakwood and both American oak (generally *Quercus alba*) and European oak (*Quercus robur* and *Quercus sessilis*) are used. During maturation additional materials are derived from the cask and re-equilibration of components already in solution also occurs. Generally, three distinct processes are believed to take place,[79] namely:

(1) Chemical interactions among substances in solution

(2) Oxidation reactions

(3) Extraction and breakdown of substances from the wood.

It is believed that the levels of esters, carbonyl compounds and acids generally increase during the period whereas the level of alcohols remains relatively static. In a recent study of bourbon maturation a small amount of ^{14}C-labelled ethanol was added to a test cask and Reazin[80] and co-workers were able to confirm these general trends. Earlier Baldwin and Andreasen[81] from the same organization had proposed that the term TBDM (total barrel derived materials) which they defined as the sum of the volatiles and the non-volatiles in an aged product, could be a useful parameter. The increase in the quantity and multiplicity of esters which takes place is perhaps the easiest to study in flavour terms. Since the constituent alcohols and acids have lower odour thresholds[57] an overall increase in aroma must result. In a study of malt whisky maturation[82] isoamyl acetate increased from 7.2 p.p.m. (at bottling strength) to 9.0 p.p.m. in 5 years, an increase of 8 odour units or 0.7 % compared to the artificial 'base'. The increase in the multiplicity of esters is believed to influence the quality of the aroma, producing a more blended effect. This can be demonstrated by the well

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[78] G. C. Williams, *Amer. J. Enol. Viticult.*, 1962, **13**, 169.

[79] A. J. Liebmann and B. Scherl, *Ind. Eng. Chem.*, 1949, **41**, no. 3. p 534.

[80] G. H. Reazin, S. Baldwin, H. S. Scales, H. W. Washington, and A. Andreasen, *JAOAC*, 1976, **39(4)**, 770.

[81] S. Baldwin and A. Andreasen, *JAOAC*, 1974, **57**, no. 4, p. 940.

[82] J. D. Gray and J. S. Swan, unpublished work.

known technique where individual components are represented by triangles whose areas are proportional to their odour potency. The nearer the outline approximates to an arc then the more blended the aroma will become (Figure 9).

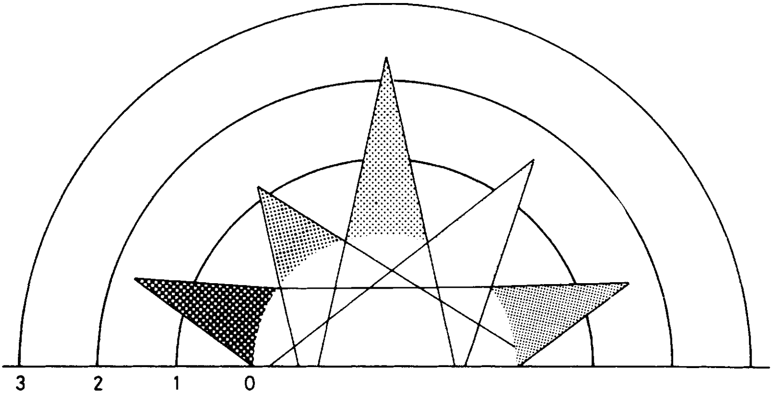

Figure 9 *Combination of individual aromas to form a blended complex*

Recently, in a study of acetal formation in rum, Misselhorn[83] has shown that acetals have lower odour thresholds than the corresponding aldehydes from which they are formed. In any event it was suggested that most acetals detected in rum are artefacts and are without importance in rum flavour.

Turning to the influence of oxidation reactions Petersen[84] in a study of wine maturation has recently shown that a vacuum builds up inside casks during maturation presumably due to the evaporation of liquid out through wood pores without a corresponding ingress of air. The amount of oxygen available to the product depends therefore on the physical soundness of the cask. Singleton[85] believes that oxygen does not pass through the timber and that an impermeable layer is formed at the interface of the oxygen and barrel contents.

For the most part the third process, *i.e.* interaction of the ethanol and wood, results in an increase in relatively non-volatile compounds such as phenolic acids, tannins, *etc.* which influence the astringency and bitterness of flavour rather than the aroma. Guymon and Crowell[86] identified diethyl succinate, 5-methyl furfural and β-methyl-γ-octalactone as substances deriving from the oak cask during brandy ageing. This latter compound, often known as oak lactone has an intense coconut-like aroma but was considered by Suomalainen[57] to have little overall impact owing to the low concentration present in matured spirits. Singleton[87]

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[83] K. Misselhorn, *Ann. Technol. Agric.*, 1975, **24**, no. 3—4, p. 371.

[84] R. G. Petersen, *Amer. J. Enol. Viticult.*, 1976, **27**, no. 2, p. 80.

[85] V. L. Singleton, Paper presented at a Maturation Symposium, Long Ashton Research Station, Bristol, 21 January 1977.

[86] J. F. Guymon and E. A. Crowell, *Amer. J. Enol. Viticult.*, 1972, **23**, no. 3, p. 114.

[87] V. L. Singleton, in 'Chemistry of Winemaking', ed. A. Dinsmoor Webb, American Chemical Society, Washington, 1974.

has shown that European oak contributes more extract and more tannin during maturation of wine but American oak contributes more flavour, although it is possible that the differing techniques for preparing the wood may play an important part in this difference.