

Role of Organic Acids in Maturation of Distilled Spirits in Oak Casks

by John M. Conner

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

and Alistair Paterson, Lorraine Birkmyre, John R. Piggott

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

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Maturation of whiskies and brandies in oak casks proceeds by reducing the perception of less desirable aromas of new distillates. During maturation, extraction of wood components increases the solubility of distillate compounds which reduces their headspace concentration above the matured spirit. The origins of this interaction are changes in aggregation of ethanol due to increases in contents of organic acids. During wood maturation organic acid concentrations in spirits increase as a result of extraction from cask wood, oxidation of ethanol and evaporation of ethanol and water. The effect of such changes was simulated using a model whisky ester in aqueous solutions of ethanol with acetic acid, oak wood extracts and acid fractions from new and matured Scotch malt distillates.

Key Words: Whisky, maturation, oak casks, organic acids.

INTRODUCTION

Throughout the world carbohydrates, notably of cereals and grapes, are fermented by yeasts to obtain alcoholic beverages some of which are subsequently distilled to yield an eau-de-vie or white spirit. In many countries distillates are then matured in wooden, typically oak, casks to produce either whiskies (from cereal distillates) or brandies (from grape distillates). The period of wood maturation produces changes in spirit character, notably accumulation of relatively non-volatile wood components and reductions in less desirable characters of new distillates - described as *soapy*, *oily* and *grassy* notes¹⁶. However, few distillate components actually disappear during maturation and the concentrations of most flavour compounds increase due to evaporation of both ethanol and water²⁰. Addition of extracted wood components to model systems and new Scotch malt distillates has been shown to change the activity, or headspace partition, coefficients of aroma compounds^{4,5}. Such effects reduce concentrations of compounds in the air above the spirits, reducing their sensory impact and improving acceptability to consumers through marked changes in character.

Potable spirits consist mostly of ethanol and water

with the flavour-active components comprising only a very small proportion of the beverage. However, only at low ethanol concentrations (<17% v/v) are aqueous ethanol mixtures homogeneous, with molecules of ethanol mono-dispersed in water³. At higher concentrations ethanol molecules cluster to reduce hydrophobic hydration. This aggregation of ethanol molecules has been shown to increase solubility of ethyl esters, reducing activity coefficients and consequently concentrations in spirit headspaces⁶.

Wood extracts have been shown to decrease the concentration at which aggregation of ethanol molecules occurs with a subsequent lowering of activity coefficients in solutions with ethanol concentrations between 5 and 30% (v/v)⁷. These reductions in activity coefficients occur at both ambient and human mouth temperatures and so would alter the release of aroma active molecules when mature spirit is consumed. Therefore, above 17% (v/v) ethanol - water, mixtures do not act as true solutions but are in effect microemulsions. Modelling of flavour release from emulsions has shown that headspace partition and interfacial mass transfer coefficients are major determinants of flavour release in the mouth⁹. Thus changes in activity or partition

coefficients produced by wood maturation will alter the release of distillate components in the glass and mouth, changing the aroma and taste of a matured spirit.

Changes in headspace partition coefficients also provide connections between physico-chemical and sensory properties of wood-matured spirits. It has been known for some years that wood maturations of distillates produce physico-chemical changes in the liquid detectable by nuclear magnetic resonance spectrometry^{1,2}, differential scanning calorimetry¹³, small-angle X-ray scattering² and mass spectrometric analyses of liquid clusters¹¹. Such studies suggest both a greater degree of non-uniform structure in aged brandies and increases in large ethanol polymer hydrates in wood-matured whiskies. In essence, changes in headspace concentrations of important ethyl esters are consistent with the presence of either more, or larger, ethanol aggregates in matured spirits, with a greater capacity for solubilising hydrophobic compounds.

Previous research on the dispersed phase formed on dilution of Scotch malt whisky had indicated that acetic acid was partly responsible for the stabilisation of these solute structures in the matured spirit⁸. No effect on headspace partition of ethyl decanoate was noted at concentrations required for stabilisation of the dispersed phase. Reductions in headspace concentrations were observed at higher concentrations (0.4 - 1.0 molar). This paper describes the further investigation of this observation.

MATERIALS AND METHODS

Ethanol - water mixtures were prepared using HPLC-grade ethanol and water purified by a MilliU10 system (Millipore UK Ltd., Watford). Ethyl decanoate (Sigma) was used as a typical hydrophobic aroma compound with a similar hydrophobicity to those responsible for immature aromas in spirits^{17,18}. Spirit samples were from the same batch of malt distillate matured for 5 years in new, charred oak casks and glass bottles (Chivas Brothers Ltd., Paisley). Activity coefficients were determined from headspace concentrations quantified by gas chromatography using a previously published method⁴.

Wood extracts were prepared by completely immersing a piece of charred American oak stave (*Quercus alba*) weighing approximately 60 g in 1 litre of 65% ethanol (v/v) at ambient temperature for 30 days. The extract was then decanted, filtered and stored at -18°C before use.

Extracts of organic acids were prepared by diluting 200 ml of spirit with 200 ml 50 mM NaOH and extracting three times with 50 ml portions of dichloromethane. The diluted spirit was neutralised and acidified with 100 ml of 1 M HCl and extracted as before with dichloromethane. These latter fractions were bulked, dried over anhydrous sodium sulphate and

evaporated to dryness. The residue was dissolved in 200 ml of 65% ethanol (v/v).

Aliphatic acids were quantified by HRGC using a Carlo Erba Mega gas chromatograph with a split-splitless injector, a 0.25 mm x 30 m CP-Wax 52 CB column (df = 0.2 µm) and flame ionisation detection. Injector and detector were at 230° and 250°C respectively. The column was operated at 50°C for 5 min following injection, increased to 240°C at 8°C min⁻¹ and then held for 5 min. Identifications and quantifications were by comparisons with extracts from standard solutions of organic acids.

RESULTS

Ethyl decanoate was selected as a typical hydrophobic flavour compound found in new Scotch malt distillates^{17,18}. To provide a simple model a 25 mg litre⁻¹ standard solution was prepared in 23% ethanol, a typical ethanol concentration for the sensory assessment of spirits¹⁵. Increases in both volatile and non-volatile (fixed) acidity are observed during maturation of distilled spirits¹² and this was simulated by the addition of acetic acid to the simplified model. Addition of acetic acid resulted in a large decrease in ethyl decanoate activity (Fig. 1). In contrast only a small increase in acetic

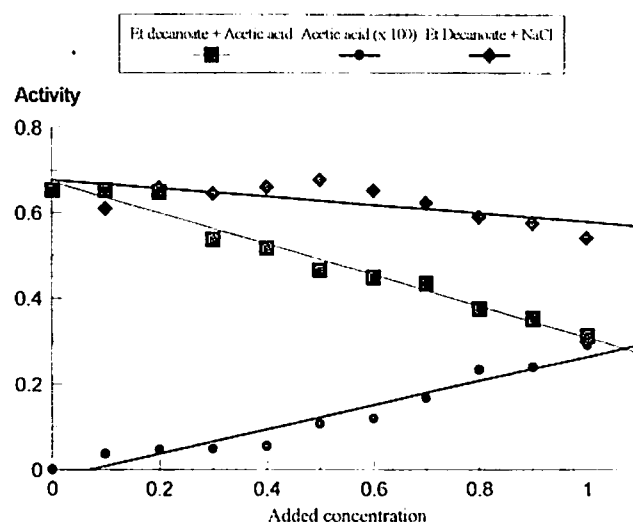


FIG. 1. Changes in ethyl decanoate activity in the presence of increasing concentrations of either acetic acid or NaCl. The activity of acetic acid (x 100) when added to the ethyl decanoate solution is also shown.

acid activity was observed. This rules out the formation of a saturated solution by the combination of acetic acid and ethyl decanoate which would result in agglomeration of ethyl decanoate and a corresponding reduction in its activity⁴. However, the activity of acetic acid determined from headspace concentrations represented the activity of only non-ionised molecules.

To test for pH and ionic effects, acetic acid was replaced with 0.01 molar oxalic acid giving a solution pH of 3. With oxalic acid no reduction in ethyl decanoate activity was observed. Addition of increasing concentrations of acetic acid to the model containing oxalic acid produced reductions in ethyl decanoate activity identical to those in the model solution without oxalic acid. The lower pH produced by oxalic acid would influence the ratio of ionised to non-ionised acetic acid but this does not affect the reduction in ethyl decanoate activity. The effect of ionic hydration on the activity of ethyl decanoate was investigated by substituting NaCl solutions for acetic acid. Concentrations up to 1 molar NaCl produced only small reductions in ethyl decanoate activity (Fig. 1). The effect of acetic acid therefore did not appear to originate from either change in pH or ionic hydration of the dissociated acid.

The effect of increasing chain length of the organic acid was investigated using an homologous series of monocarboxylic acids (Fig. 2). This showed that the acid

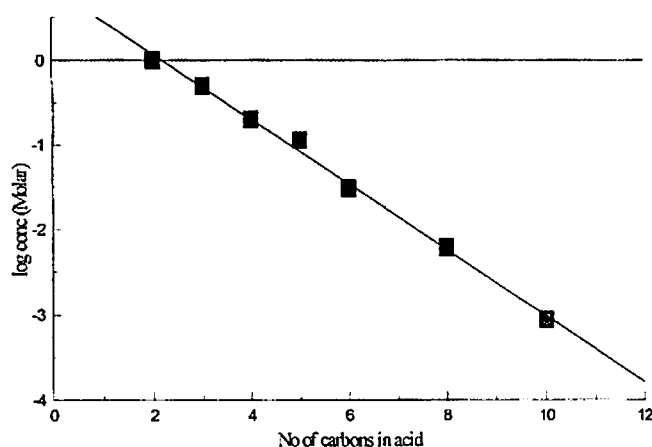


FIG. 2. The logarithm of the concentration of organic acid required to half the activity of ethyl decanoate standard solution against the number of carbons in the acid.

concentration required to decrease ethyl decanoate activity to 50% of the original or control value gave a log-linear correlation ($R^2 = 0.995$) with the number of carbon atoms in the acid. This relationship however, held up only to decanoic acid, as dodecanoic, tetradecanoic and hexadecanoic acids, even at saturating concentrations, had no influence on ethyl decanoate activity.

The mechanism of this interaction was studied further by calculating the infinite dilution mole fraction activity coefficient of ethyl decanoate at differing alcoholic strengths in range 2.5 to 40% ethanol (Fig. 3). Activity coefficients were determined at 37°C to demonstrate that interactions between distillate and organic acids had effects at mouth temperature and

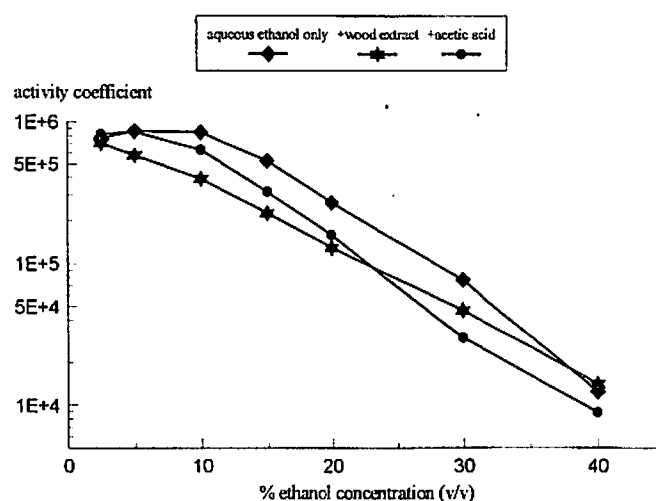


FIG. 3. The effect of ethanol concentration on the activity coefficient of ethyl decanoate at 37°C for binary mixtures of ethanol and water and mixtures containing wood extract and 1 Molar acetic acid.

could therefore alter the release of volatiles during consumption. At 37°C, binary mixtures of ethanol and water gave significant decreases ($p < 0.05$) in ester activity coefficients at ethanol concentrations $> 10\%$ (v/v) (Fig. 3). When 1.0 molar acetic acid was added to such mixtures, a significant decrease ($p < 0.05$) in ester activity coefficient was observed between 5 and 10% ethanol (v/v) with further reductions in the range 15–40%. To simulate an actual spirit maturation the experiment was repeated using dilutions of a 65% ethanol (v/v) extract of charred American white oak (*Quercus alba*). In the presence of wood extractives, decreases in ester activity coefficient were observed from 2.5% ethanol (v/v) although the subsequent rate of decrease in activity coefficient was lower than with acetic acid.

To clarify contributions of the acids, specific acid fractions were prepared from the same batch of malt distillate matured for 5 years in glass bottles (new distillate) and new, charred American oak casks (mature distillate). Dilutions of each acid fraction to between 2.5 and 40% ethanol were prepared to determine ethyl decanoate activity coefficients at 25°C. In binary mixtures of ethanol and water, significant decreases ($p < 0.05$) in activity coefficient were observed from 15% ethanol (v/v) (Fig. 4). Ethanol has a small negative enthalpy of solution¹⁰ which results in lower critical concentrations for aggregation as the solution temperature increases. This, however, produces only small differences in activity coefficients between 25 and 37°C⁹. For the acid fraction of the new distillate, a significant decrease in ester activity coefficient was observed between 5 and 10% ethanol, with further reductions at 15 and 20% ethanol ($p < 0.05$). When the acid fraction from matured whisky was substituted for that of the new distillate, similar but greater reductions

in ester activity coefficient were observed (Fig. 4). Analyses of the two extracts showed that no individual organic acid was present at a concentration sufficient to influence ester activity coefficient (Table I). Thus the observed effect must be due to the sum of individual acid contributions.

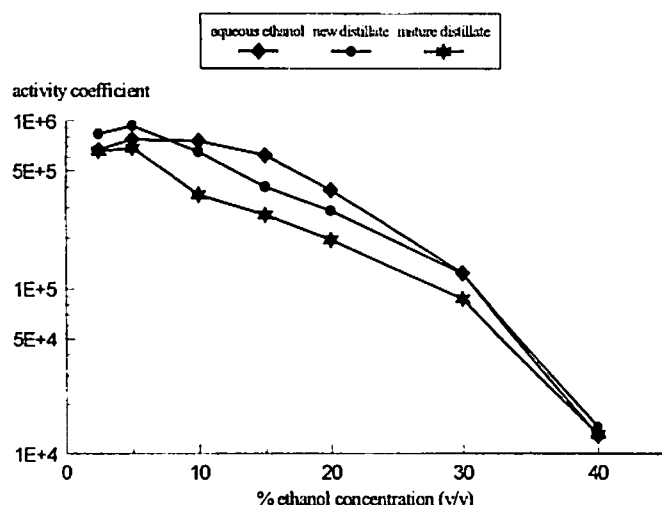


FIG. 4. The effect of ethanol concentration on the activity coefficient of ethyl decanoate at 25°C for binary mixtures of ethanol and water and mixtures containing the acid fractions of new distillate and mature spirit.

TABLE I. Concentrations of organic acids (mg litre⁻¹) present in acid fractions of new distillate and mature whisky.

Acid	New Distillate	Matured Whisky
acetic	nd	nd
3-methylbutanoic	5	7
hexanoic	7	9
octanoic	16	22
decanoic	13	18
dodecanoic	10	12

nd = not detected

DISCUSSION

Our experiments show that the presence of organic acids influences the aggregation of ethanol in aqueous solution. This is demonstrated by marked reductions in headspace partition coefficient of ethyl decanoate. Polarity fractionation of distilled spirits showed that

compounds responsible for immature aromas in spirits are concentrated in fractions with a similar hydrophobicity to ethyl decanoate^{17,18}. Reducing the release of such components into the headspace would lessen the sensory impact not only in static systems, such as during nosing of spirit headspaces, but in the dynamic situation of the liquid in the mouth during consumption. During maturation in oak casks, increases in both volatile and non-volatile (fixed) acidity are observed¹². Increases in acetic acid concentration comprise the largest component, being both extracted from wood and formed by oxidation of ethanol¹⁹. Further increases in concentrations of organic acids in distillates must occur as a result of the evaporation of ethanol and water²⁰. Extraction from stave wood also yields octanoic and decanoic acid, from breakdown of wood lipids, and the dicarboxylic acids succinic, adipic and methylsuccinic acids¹⁴. Gallic, vanillic, syringic and ellagic acids are also extracted from the lignin and tannin components of wood¹⁶. Only aliphatic acids were quantified by the gas chromatographic analysis, the effect of phenolic and dicarboxylic acids on ethanol aggregation remains to be determined.

The precise nature of the interaction is also unclear. When monodispersed in water, the nonpolar groups of ethanol are thought to be surrounded by an 'elasticated net' of structured water molecules²². Above the critical point, ethanol molecules aggregate to reduce the non-polar surface area in contact with the water. Aggregation occurs (at 25°C) at a ratio of between 16 and 20 molecules of water to 1 molecule of ethanol³ but NMR studies indicate a dynamic hydration number of between 7 and 9 for ethanol²¹. It therefore appears that aggregation occurs when approximately 50% of water molecules are involved in 'hydrophobic hydration'. The interaction between ethanol and acids may therefore arise because acids behave as soluble hydrocarbons and tie up a proportion of the available water for hydration and so induce aggregation of ethanol at lower concentration. Alternatively ionic hydration of the polar acid group may affect the balance of water available for 'hydrophobic hydration' and so reduce the critical concentration. However, the strong relationship between the interaction and the size of the acid hydrocarbon chain and lack of affect of purely ionic components on a mole for mole basis suggests the former explanation to be the more likely.

CONCLUSIONS

The influence of organic acids on ethyl decanoate headspace partition coefficient is a clear demonstration of a direct relationship between physico-chemical changes of distillate and concentrations of hydrophobic aroma compounds in headspaces above spirit samples. Polarity fractionation of distilled spirits has shown that compounds responsible for immature aromas in spirits

are concentrated in hydrophobic fractions^{17,18}. Increasing the solubility of such components would lessen the sensory impact not only in static systems, such as during nosing of spirit headspaces, but in the dynamic situation of the liquid in the mouth during consumption. The air - liquid partition coefficient has been identified as a key determinant for the release of flavour components in such situations⁹. Changes in the aggregation of ethanol are thus likely to cause reductions in headspace partition coefficients of compounds responsible for the immature character of new distillates and reduced perceptions of immaturity as wood ageing proceeds. This appears to be a key process in determining the aroma and flavour of wood matured spirits.

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