The reduction of α-acetolactic and α-acetohomolactic acids is presumably catalysed by enzymes of *Saccharomyces uvarum*, the main fermenting yeast present in these sulphited fermentations.

An α-ketoglutaric reductase may also be present, since a decrease in this acid and the presence of its reduction product α-hydroxyglutaric acid have been noted in some fermentations. Such an enzyme has been reported in *Achromobacter* sp.[15]

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INSTABILITY IN POTABLE SPIRITS. I.—Scotch Whisky

By L. A. WARWICKER

Instability in spirits is partly inherent, partly caused by contamination during maturation and partly due to bad filtration techniques. Instability occurs as deposition with metallic contamination and alteration of the pH to critical values. It is distinct from the formation of 'inks'. Chill-proofing is not sufficient in itself to provide a stable product if sufficient contamination occurs afterwards. Ion-exchange in the H^+ form removes an instability factor.

Introduction

Manufacturers of potable spirits have found difficulty in obtaining a ' bright ' product or one that will retain its brightness for several months. A typical instability is ' greying ' (the name given when the spirit develops a cloudiness or haze), which is produced when the spirit is subjected to low temperatures. The process of haze production is reversible since on raising the temperature of the spirit the haze will disappear providing that no deposition has occurred. If the spirit has developed a deposit it is said to be ' thick ', and complete reversal is very unlikely.

The purposes of this investigation were to determine the causes of such instability and to suggest means by which the stability of spirits might be improved.

Instability in a spirit could be an inherent quality of the individual spirit concerned, it could be caused by contamination during manufacture or it could be developed during maturation. During this investigation particular interest was taken in this question.

Throughout this paper Scotch whisky is to be understood as the ' blended ' product which

is commercially available and not a ' straight ' whisky which has very limited sale because of its heavy character. Blended Scotch whisky is an approximately 50/50 mixture of ' malt ' and 'grain ' whiskies. A description of the production of Scotch whisky is given by Valaer,[1] while maturation of American whisky is covered by several authors.[2-4]

Experimental

A. *Nature of the deposit and supernatant liquor*

The greenish-black fluffy material in five bottles of whisky was allowed to settle and the bulk of the supernatant liquor decanted off. The residues were all placed in one bottle to settle out and the supernatant liquor removed carefully through a capillary tube attached to a vacuum line. The deposit was transferred with a little water to a weighed crucible and dried at 100° to constant weight. The deposit was then dry ashed in an oven at 500° for 24 h. and reweighed. The white residue was extracted twice with a mixture of 1 ml. of water and 0·5 ml. of 0·1N-HCl, with heating. The extract was filtered through a Whatman No. 41 paper and made up to 5 ml. in a standard flask. The colourless solution was analysed by the following methods :

(a) *Iron:* spectrophotometrically with thioglycollic acid, the red colour being measured at 530 mμ.

(b) *Copper:*[5] spectrophotometrically with bis-cyclohexanone-oxalyldihydrazone, the blue colour being measured at 595 mμ.

(c) *Calcium and magnesium:*[6] by titrations with EDTA and Eriochrome Black T as the indicator for the total calcium and magnesium, and murexide for calcium alone. The determinations were scaled down so that 0·5 ml. of the extract solution was used in 10 ml. of water, the standard EDTA solution being added from a microburette. The magnesium content was calculated from the difference in the titres.

(d) *Total acidity:* by the official method.[7]

(e) *Total cationic species* (T.C.S.)*:* This was determined on a 12-cm. column of Zeo-Karb 225 (Permutit) in the H$^+$ form contained in a 0·5 × 18 cm. Pyrex tube. The column was rinsed with 5 ml. of the supernatant liquor to remove any residual water, and a further 50 ml. were then passed through the column, fractions of 10–11 ml. being collected at a flow rate of 1 ml./min. Ten ml. of each fraction were titrated against 0·1N-NaOH as in (d).

The difference between the total acidity before and after ion-exchange is a measure of the total cationic species present.

(f) *pH* by a direct reading instrument (EIL model 24 A) using a glass electrode in conjunction with a calomel electrode.[8]

B. *Analysis of whisky used for experiments*

Gallon samples of B. 294 and B. 297 whisky were filtered through membrane filters to ensure a bright filtrate and samples of each analysed.

(a) *Alcohol:* by distillation of a 75-ml. sample and determination of the density of the distillate at 20°.

(b) *Potassium and sodium:* by a direct measurement with an EEL flame photometer and standard solutions of potassium and sodium salts. Under the conditions of this experiment the accuracy was ±2% for K and ±3% for Na.

(c) *Tannin:* spectrophotometrically directly on the whisky using the Folin–Denis reagent by the method of Pro.[9]

(d) *Fusel oil:* A 25-ml. sample was refluxed with *m*-phenylenediamine for 15 min. to fix any aldehydes, then for a further 30 min. with an excess of 0·1N-NaOH to hydrolyse the esters. The sample was then distilled into a 25-ml. standard flask and the distillate made up to volume with water. Aliquots were treated with 4-hydroxybenzaldehyde-3-sulphonic acid to produce a red colour as in the method of Mathers & Schoeneman.[10]

(e) *Caramel and colour:* The caramel content was calculated from the amount added to the known bulk gallons of each blend. The colour was determined spectrophotometrically at 430 mμ.[11]

(*f*) *Calcium, magnesium, iron, copper and phosphorus:* Samples (100 ml.) were evaporated and ashed at 500° for 24 h. The ash was extracted with water containing a few drops of AnalaR conc. HCl. The volume was made up to 25 ml. and aliquots of 2 or 3 ml. were tested by the methods described above for calcium, magnesium, iron and copper. The phosphorus was determined spectrophotometrically at 830 mμ by the method of Beck & Pro[12] scaled down to use a 10-ml. aliquot. Under the conditions of these experiments the accuracy was found to be $\pm 1\%$ total iron; $\pm 1\%$ copper; $\pm 20\%$ magnesium; $\pm 10\%$ calcium; $\pm 5\%$ phosphorus (as PO_4^{3-}).

(*g*) *Total acidity, total cationic species and pH* were determined as described above.

C. *Addition experiments*

Samples were inspected daily for the first 4 weeks, then weekly for the next 2 months and then monthly.

(*a*) *General additions to whisky* (B. 297)

Sufficient aqueous solution of the following : AnalaR grade $FeSO_4,7H_2O$, $CaCO_3$, K_2CO_3, Na_2CO_3, Cu acetate ($+1H_2O$) and standard laboratory grade $FeCl_3,6H_2O$, $MgCO_3$, $SnCl_2$, Zn acetate ($+2H_2O$) were added to increase the content of the cation by 5 p.p.m. Other additions were gallic acid, tannin as *m*-digallic acid, spirit caramel, paxarette (a sweet Spanish sherry used to sweeten casks), and protein (egg albumen).

(*b*) *Cationic additions to whisky* (B. 294 and B. 297)

To 50-ml. samples of whisky were added various salts (see Table II) in amounts to increase the cation concentration by 5 or 10 p.p.m.

(*c*) *Anionic additions to whisky* (B. 294 and B. 297)

A similar experiment to C (*b*) was carried out with AnalaR Na_2CO_3, NaCl, Na_2SO_4, Na_2 pyrophosphate and KH_2PO_4 added to increase the anion concentration by 5 or 10 p.p.m.

(*d*) *Cationic and anionic additions to fusel oil-free alcohol*

One litre of ethanol (96% by vol.) was fractionally distilled through a column packed with Dixon-Rings,[13] the column being first flooded by total reflux and the distillate collected at 78° at a rate of 1 ml./min. The first 300 ml. of distillate were discarded as they might have contained aldehydes. The next 350 ml. were taken as being free from aldehydes and fusel oil, the fusel oil being left in the residue. This fusel oil-free fraction was diluted to 70° Sykes with distilled water and 50-ml. samples used for the addition experiments as described above but with increases of anion or cation concentration of 10 p.p.m. only.

(*e*) *Iron and tannin additions to whisky* (B. 294)

To 50-ml. samples were added 0 to 1·4 ml. of an aqueous (slightly acid) solution of AnalaR ferric ammonium sulphate (0·2153 g./500 ml.), followed by distilled water to bring the total volume in each case to 51·4 ml. Two samples were given a solution of ferric ammonium sulphate ten times stronger than before, added to bring the total iron concentrations to 2·6 p.p.m. and 3·6 p.p.m. when the total volume had been up to 51·4 ml. with water.

Aqueous solutions of tannin (as tannic acid) (50 or 100 p.p.m.) were added to 50-ml. samples in amounts of 0·08–0·48 ml., the volumes made up to 50·48 ml. with water. The final solutions had tannin contents of 118–127·5 p.p.m.

(*f*) *Addition of alcoholic and aqueous wood extracts*

Shavings were planed off staves of an oak sherry-butt from which the dirt had been removed (by planing), and 180 g. were placed in a Soxhlet thimble (17 × 5½ cm.) which had been soaked in strong ethanol for several hours. The whole was extracted in a Quickfit extraction apparatus 600 RJSX for 24 h. with 750 ml. of fusel oil-free alcohol, and the extract used to extract another 180 g. of shavings in the same way. The extract was concentrated to 150 ml. in a vacuum and filtered through a membrane filter. The filtrate was analysed for tannin, iron, copper,

calcium and magnesium and its pH determined. The solid left in the thimble was air-dried and weighed to give an approximate loss of weight.

A similar extraction was carried out with distilled water but the apparatus had to be lagged to prevent heat losses. The extract was concentrated as before but difficulty was found due to frothing. The concentrated extract was analysed in the same way as the alcoholic extract.

To pairs of 190-ml. samples of B. 294 and B. 297 whisky were added 5 ml. of fusel oil-free alcohol, 5 ml. of alcoholic extract, or 5 ml. of aqueous extract. A fourth pair were coloured with spirit caramel to a dark rum colour and 5 ml. of alcoholic extract were added.

(g) Additions to ‘ doubly cation-exchanged ’ whisky

An ion-exchange column twice the size described in A (e) was converted to the H^+ form and rinsed with 15 ml. of whisky. A further 275 ml. were passed through the column at 2–3 ml./min., the column washed with water, regenerated as before and 15 ml. of the filtrate used to rinse it. The remainder of the filtrate was passed through the column a second time, to give ‘ doubly cation-exchanged ’ whisky.

Additions were made to 50-ml. samples of doubly cation-exchanged whisky : (1) 0·1N-NaOH until the pH was approx. 5 ; (2) the pH was adjusted to 5 with 10% aq. NH_3 ; (3) sufficient of a 200 p.p.m. solution of magnesium acetate to increase the magnesium content by 10 p.p.m. ; (4) 3–4 drops of the alcoholic oakwood extract added and the pH adjusted to approx. 5 with 0·1N-NaOH (all pH determined as described in section A).

(h) Addition to chilled whisky

Whisky at 70° proof was kept at —15° for 6 days and filtered in the cold. To a 50-ml. sample of the filtrate were added 2·5 ml. of an aqueous solution of magnesium acetate (200 p.p.m. Mg) to increase the magnesium content by 10 p.p.m. A control experiment was set up using 2·5 ml. of water. Duplicates of the above experiments were set up using a portion of the whisky which had not been chilled, but filtered at the same time and in the same way.

(i) Addition of fusel oil to aqueous alcohol

Genuine fusel oil from a ‘ grain ’ whisky distillation was added to pure aqueous alcohol at 110·0° proof in amount approximately that found in practice (0·8 g./l.). The mixture was reduced to 70° proof with distilled water and 2·5 ml. of aqueous magnesium acetate solution (200 p.p.m. Mg) were added to each of two 50-ml. samples. Controls were set up with 2·5 ml. of water in place of magnesium acetate solution. One sample and a control were placed in a cold tank at —5° for several days. The other solutions were kept at room temperature.

D. Alteration of pH

The pH of pairs of 50-ml. samples of whisky B. 297 was adjusted to definite values between 4·45 and 11·55 by the use of N- and 0·1N-NaOH and 10% aq. NH_3. The pH of each sample was checked by the pH meter and the samples inspected every day for 1 month and then at weekly intervals.

An experiment was carried out with fusel oil-free alcohol reduced to 70° Sykes, with distilled water, to give pH 8·5. The pH of a 50-ml. sample was adjusted to 4·96 with aqueous acetic acid. To another sample spirit colouring was added and the pH adjusted to 4·92 (aqueous acetic acid). To a third sample 3–4 drops of the alcoholic extract of oakwood were added and the pH adjusted to 4·95 as before. The samples were inspected every 2–3 days for one month and then monthly.

A further experiment was carried out on alcohol with added fusel oil as prepared in section C (i). To a 50-ml. sample 2·5 ml. of aqueous magnesium acetate solution (200 p.p.m. Mg) were added and the pH adjusted to 5·0 with a few drops of dilute acetic acid. A control also at pH 5 was set up using water in place of the magnesium acetate.

Results

The dry weight of deposit used was 20·2 mg. (dried at 100°) of which 5·3 mg. was left after being ashed at 500°. The ash contained iron 3·0%, copper 3·2%, calcium 7·5%, and magnesium 7·2%.

The supernatant from the deposit had a total acidity equivalent to $2 \cdot 3 \times 10^{-3}$N, a T.C.S. of $1 \cdot 65 \times 10^{-3}$N and pH $5 \cdot 05$. Samples taken before and early in the filtration showed a decrease in total acidity from $2 \cdot 8 \times 10^{-3}$N to $2 \cdot 1 \times 10^{-3}$N, while the T.C.S. increased from $0 \cdot 6 \times 10^{-3}$N to $4 \cdot 85 \times 10^{-3}$N with an increase in pH from $4 \cdot 37$ to $5 \cdot 9$. The complete filtrate after being mixed showed only slight differences from the original before filtration.

These results show that 75% of the deposit was organic and the pH of the supernatant whisky was higher than normal as the cationic content had been doubled.

The analysis of whisky blends 294 and 297 showed, alcohol 70° Sykes ($40 \cdot 9\%$ by vol. at 20°), total acidity $2 \cdot 4 \times 10^{-3}$N, T.C.S. $1 \cdot 0 \times 10^{-3}$N and tannin 120 p.p.m. Other results (blend 294 first) in p.p.m. were : phosphate ($9 \cdot 0$, $10 \cdot 0$) ; fusel oil (820, 770) ; caramel (744, 692) ; copper ($0 \cdot 3$, $0 \cdot 4$) ; iron ($0 \cdot 5$, $0 \cdot 2$) ; calcium ($5 \cdot 5$, $5 \cdot 0$) ; magnesium ($1 \cdot 7$, $2 \cdot 0$) ; potassium ($9 \cdot 0$, $10 \cdot 0$) ; sodium ($15 \cdot 5$, $16 \cdot 8$). The colours were $7 \cdot 62$ and $7 \cdot 70$ units and the pH $4 \cdot 35$ and $4 \cdot 31$ respectively.

Since it was known that excess of calcium and magnesium would cause deposition it was concluded that additions of the ions in the presence of acid had inhibited deposition. Consequently these and other ions were added as acetates or sulphates, which did not reduce the pH and in most cases increased it.

Results for the experiments for whisky samples to which the various additions had been made are detailed in Tables I and II. It was found that there was no deposition in 6 months with the following additions of added anion (p.p.m.), the pH values found being shown in brackets : NaCl 10 ($4 \cdot 32$), 5 ($4 \cdot 28$) ; NaNO$_3$ 10 ($4 \cdot 32$), 5 ($4 \cdot 36$) ; Na$_2$CO$_3$ 10 ($4 \cdot 61$), 5 ($4 \cdot 42$) ; Na$_2$SO$_4$ 10 ($4 \cdot 33$), 5 ($4 \cdot 35$) ; Na pyrophosphate 10 ($4 \cdot 44$), 5 ($4 \cdot 37$) ; KH$_2$PO$_4$ 10 ($4 \cdot 27$), 5 ($4 \cdot 32$).

Table I

pH and observations for general additions to whisky B. 297

Sample	pH	Observation	Sample	pH	Observation
None	4·35	No deposit after one year	Zn²⁺	4·79	Typical deposit in 2 days ; darkened after 3 months
Fe²⁺	4·16	Darkened after few days			
Fe³⁺	3·97	Darkened at once	Sn²⁺	4·14	No deposit after one year
Cu²⁺	4·30	No deposit after one year	Albumen	4·57	Deposition at once, not typical
Ca²⁺	3·30	,, ,, ,, ,, ,,	Gallic acid	4·33	No deposit after one year
Na⁺	4·16	,, ,, ,, ,, ,,	Tannin	4·30	,, ,, ,, ,, ,,
Mg²⁺	3·73	,, ,, ,, ,, ,,	Paxarette	4·36	,, ,, ,, ,, ,,

Table II

Observations after cationic and anionic additions to whiskies
B. 294 and B. 297

Cation	Anion	Increase in concn., p.p.m.	pH	Observation
NH₄	acetate	10	4·75	No deposit after 1 year
NH₄	acetate	10	4·91	,, ,, ,, ,, ,,
Li	chloride	10	4·10	,, ,, ,, ,, ,,
Na	acetate	10	4·63	,, ,, ,, ,, ,,
Na	acetate	10	4·61	,, ,, ,, ,, ,,
Na	carbonate	10	4·61	,, ,, ,, ,, ,,
Ca	acetate	10	4·73	,, ,, ,, ,, ,,
Mg	acetate	5	4·67	Deposit after 9 weeks
Mg	acetate	5	4·70	,, ,, 2 ,,
Mg	acetate	10	4·95	,, ,, 3 days
Mg	acetate	10	4·97	,, ,, 2 ,,
Cu²⁺	sulphate	10	4·37	No deposit after 1 year
Sn²⁺	chloride	10	3·99	,, ,, ,, ,, ,,
Zn	acetate	5	4·79	Deposit after 2 days
Zn	acetate	5	4·50	Slight deposit 13½ weeks
Zn	acetate	5	4·55	,, ,, 12½ ,,
Zn	acetate	10	4·61	Deposit after 11½ weeks
Zn	acetate	10	4·67	,, ,, 2 ,,
Al	sulphate	5	3·75	Orange deposit after 2 weeks
Al	sulphate	5	3·72	,, ,, ,, ,, ,,
Al	sulphate	10	3·70	,, ,, within 3 days
Al	sulphate	10	3·85	,, ,, ,, ,, ,,

Preliminary experiments showed that iron will darken the colour, so the effect of increasing the iron content from 0·6 to 3·6 p.p.m. was studied, by addition of ferrous ammonium sulphate in a very small amount of dilute H_2SO_4. When the tannin content was increased from 118 to 127·5 p.p.m. the darkening produced could not be detected by the human eye. With 2·6 p.p.m. of iron the colour was darker than that in the control experiment, while with 3·6 p.p.m. the colour became greener and obviously darker. No deposition occurred in any of these experiments even after one year.

When the iron/tannin ratio (p.p.m.) was varied from 57 to 408 the colour intensity decreased from 7·42 to 6·43 units. The pH was not altered appreciably until the iron/tannin ratio was 113.

Analysis of the aqueous and ethanolic extracts of oakwood showed the presence of less than 1 p.p.m. of iron, copper and magnesium. Calcium was not detected in the ethanolic extract, but in the aqueous extract there was 7 p.p.m. The aqueous and ethanolic extracts had pH 3·22 and 5·80 and tannin contents of 1900 p.p.m. and 740 p.p.m. respectively. The results in Table III show that the barrel extractives contribute to deposition and that the double ion-exchanging has removed it.

Both the chilled and non-chilled whisky samples with added magnesium acetate solution showed a typical deposit after 3 days, whilst the controls remained bright. The amount of deposit formed with the chilled whisky was less than with the non-chilled, however.

The addition of fusel oil to alcohol followed by further additions of water or aqueous magnesium acetate gave no deposit or haze at room temperature, but those kept in a cold tank for 10 days showed only a very slight haze.

The rate of deposition increased as the pH increased from 4·5 to 4·9, but from 6·0 upwards no deposition occurred even after 5 months. A similar experiment with 10% aq. NH_3 gave no deposit even at pH 4·9 after 5 months.

In order to deduce whether the ionic and other additions were reacting with the aqueous alcohol present, similar experiments were carried out on fusel oil-free alcohol at 70° Sykes in place of whisky. Increase in the concentration of the particular ion by 10 p.p.m. (except Zn acetate 25 p.p.m.) gave deposition after 3 and 5 days, respectively, with Al^{3+} and Fe^{2+}, but was not typical in either case, Al^{3+} giving a white and Fe^{2+} a red-brown deposit. The cationic additions gave pH in the range 3·85 to 6·70, and the anions in the range 5·22 to 6·75.

In the experiments with fusel oil-free alcohol with the pH adjusted to 4·92–4·96 with acetic acid, no deposits developed in 5 months without or with added spirit colouring, but when the alcoholic extract of the oak wood was added, a very faint white suspension was found after 2 days, which settled into a very slight granular deposit after 3 weeks, but there was no typical deposit after 5 months.

The addition of magnesium acetate to alcohol with added fusel oil did not produce a deposit on adjusting the pH to 5·0.

Discussion

Collection of the deposit by filtration was impossible, while centrifuging after removal of the bulk of the supernatant liquor yielded only a few milligrammes. Microscopical examination of the deposit showed that it consisted of aggregated oily particles which were easily dispersed. Since there was difficulty in obtaining sufficient deposit, consideration was given to the possible variations that might occur in the whisky during maturation and on storage until it is bottled.

Table III

Observations on doubly hydrogen-ion-exchanged whisky [see text under C (g)]

Sample	pH	Observation
Original B. 297 whisky	4·31	No deposit after 6 months
B. 297, doubly H+ exchanged	3·50	,, ,, ,, ,, ,,
,, ,, ,, + NaOH	5·03	Very slight granular deposit after 2 weeks
,, ,, ,, + aq. NH3	4·96	,, ,, ,, ,, ,, 3 ,,
,, ,, ,, + Mg acetate	3·80	Very slight haze, no deposit after 6 months
,, ,, ,, + alcoholic extract, then NaOH	4·96	Deposit in 4 days

The analyses of the deposit and supernatant liquor indicate that the bulk of the deposit is organic. The increase in the pH on filtration shows that there is replacement or removal of an acidic part of the whisky. The blend giving the deposit was filtered several years ago. Since then the filter-pads have been acid-washed by the manufacturers to remove as much extractable magnesium as possible. This washing is the direct development from the discovery that brandy subsequently ' throws a deposit ' if sufficient magnesium is extracted from the filter-pads. This extraction explains why many spirits when filtered ' bright ' into a bottle subsequently throw a deposit. Refiltering the cloudy spirit until ' bright ' extracts more material from the filter-pads. Consequently the deposit is formed in an even shorter time than before although the material is ' bright ' when put into bottle for the second time. Calcium pick-up in wines from filter-pads and filter-aids is mentioned by De Soto & Warkentin.[14]

Old ideas in the spirit trade were that any deposit was due to the formation of ' inks ' (iron gallate) by excess iron with tannins extracted from the wood during maturation. The experiments in which the iron/tannin product ratio was varied have shown that no deposit is formed even when it is increased to nearly seven times the normal value, although darkening does occur as the iron concentration increases. In a severe case of iron contamination (16 p.p.m.) caused by the presence of a glass ' blister ' in the bottle used for storage in which a piece of cast iron was enclosed, and the bursting of the ' blister ', the contents were very black in colour but there was no deposit.

Aluminium and ferrous iron give a precipitate with pure aqueous alcohol, probably due to hydration of the Al and the oxidation of the Fe with precipitation of $Fe(OH)_3$. Only Mg and Zn of the ions tested will aid deposition in whisky, due to factors other than the alcohol and water present. The rate of deposition can be due to the amount of ions added and/or the corresponding increase of pH. Addition of sodium carbonate solution to whisky altered the pH to the critical value for deposition with Mg and Zn, but actually no deposition occurred, so the deposition cannot be a purely pH effect. This is further exemplified by the addition of aqueous NH_3 not producing deposition even at the critical pH. Experiments to alter the pH show that the critical pH for deposition are about 4·90 and between 7·0 and 9·8 when NaOH is used, but not when aq. NH_3 is used. Table III shows that after removal of metallic ions and replacing them by H^+, NaOH will no longer cause deposition, neither will Mg ions when added, even though in the former the pH was at the critical value. However, when alcoholic wood extract is added and then NaOH, a deposit is formed. Hence the double H^+-exchange has removed something from the original whisky which is part of or aids deposition. The fact that the addition of wood extract and adjustment to pH approx. 5·0 did not give a typical deposit with fusel oil-free alcohol, shows that the NaOH caused deposition of some factor from the added extract. The experiments involving alteration of pH and addition of magnesium acetate to alcohol with added fusel oil gave no deposition, even when cooled to —5° for 10 days. This suggests that fusel oil alone is not directly concerned in the deposition process.

Walter[15] showed that the corrosion of metals by alcoholic liquids depends on the acid content, the type of metal, the period of contact and the temperature. He also showed that alcoholic liquids (40–50% by volume of alcohol) attack iron more easily and zinc, copper, aluminium, tin and bronze less easily.

The laboratory process of extraction of the wood was probably more thorough than the 4 years' natural extraction by maturation. The extracts have a high tannin content as expected, and in the aqueous extract a very low concentration of metals except calcium. Since the addition of aqueous extract did not give deposition, but the alcoholic extract did, it is concluded that the latter contains a factor which causes or aids deposition. It is most likely that the alcoholic extract has water-insoluble components which on addition to whisky come out of solution. This is supported by Boruff & Riutschof[16] who showed that for aged American whiskies barrelled at proofs higher than 110 U.S.p. there is a slight tendency to show higher turbidities when reduced to American bottling proofs. During maturation the alcohol content falls and alcohol molecules diffuse through the wood by capillary attraction. During this time the total solids increase, showing that extraction has taken place.[3, 4] The experiment in which whisky was coloured to a dark rum standard with spirit caramel, showed that the deposit did not remove colour from the whisky (which indicates that there is no fining action).

Braus *et al.*[17] identified a haze producer in American whisky as sitosterol β-D-glucoside and traced its origin to the white oak wood used for barrels. The wood extracts described in our experiments did not, however, give positive results for a steroid with the Liebermann–Burchard, Salkowsky–Hesse or Tortelli–Jaffe tests.

Conclusions

From the experimental work performed and the nature of the deposit it is concluded that the formation of ' inks ' is not the cause of deposition in whisky, but extraction of magnesium salts from filter-pads and filter-aids contributes to the formation of a deposit. Similar contamination with zinc and aluminium salts will give a similar result. Chill-proofing with subsequent filtration will improve the stability of whisky providing there is no contamination during filtration. The development of the deposit and the rate of deposition depend upon the pH and temperature. A critical pH value for a particular blending of Scotch whiskies is 4·5, above which deposition occurs within a few days. A factor, probably a type of tannin, is extracted from the wood during maturation and is subsequently deposited when a sufficient concentration of certain metals are present and the pH is above the critical value. Hydrogen-ion exchange removes a factor causing instability because above the critical pH additions other than wood extract do not form a deposit.

Acknowledgments

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