

Acknowledgments

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INSTABILITY IN POTABLE SPIRITS. III.*—Gin and Vodka

By L. A. WARWICKER†

For good quality gin and vodka a 'clean' spirit is essential. Prolonged contact with a number of metals, or contamination with metallic salts, is to be avoided. There is no critical pH for the formation of a deposit as in other potable spirits. The deposit formed in vodka is calcium carbonate, but deposits of calcium and magnesium sulphate and magnesium carbonate are also possible. The solubility of calcium carbonate in different concentrations of alcohol is compared with values for Russian vodka and the effect of large concentrations of other ions is considered. The use of demineralised water is recommended for both gin and vodka. Where this is not possible, careful monitoring of softened water is essential.

Introduction

Gin and vodka are potable spirits which do not require maturing before being consumed. Some Polish vodka is left in Tokay casks and one London gin is left in wood to mature. Both

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gin and vodka may throw a white deposit which is essentially different from those from potable spirits matured in wood. Gin may develop a blue-coloration,¹ but this has not been observed in vodka.

Gin originally came from Holland and became increasingly popular in Britain. London gin or London dry gin is an unsweetened gin, which in fact is made in many parts of the world. Old Tom is a gin sweetened with sugar-syrup. Lemon, orange and sloe gins are classed as liqueurs, but are basically gin with various additions. There are three major ways to make gin :

- (i) by a straight distillation of the spirit with botanicals. The distillate is then reduced to bottling strength with water ;
- (ii) by a straight distillation of the spirit with botanicals, but only collecting a fraction of the distillate so that it is an over-proof concentrate. The concentrate is then mixed with more strong spirit and then reduced to bottling strength with water ;
- (iii) by adding essential oil and flavourings to spirit and then reducing to bottling strength with water. This is 'cold compounding'.

In Czechoslovakia gin is manufactured commercially from the fermentation of the dregs from crushed juniper berries by specially nurtured yeast.²

The principal addition for gin is juniper, but many other botanicals are used including angelica, orange-peel, cassia and coriander, the ingredients used and the formula being each distiller's closely kept secret. To produce a uniformity of product, besides having a 'clean' alcohol, a careful check must be kept on the botanicals.^{3, 4} Rosenblatt⁵ indicated four factors which must be checked, viz., (1) moisture content, (2) acid number, (3) volatile oil content, (4) *n* of the oil as well as the physical appearance. Levin⁶ states that acidity of gin botanicals is of little importance in the quality of gin distillations.

Vodka, which is chiefly made in Russia, Poland and Finland, has become increasingly popular in Britain and the U.S.A., where considerable quantities are now produced. It is generally made from grain-spirit, but molasses spirit is sometimes used. Russian vodka is prepared by passing the clean spirit over a specially activated wood charcoal. Generally no additions are made to vodka, although in some Scandinavian countries a herbal extract is added. To comply with British law, vodka must have something added to class the process as a 'compounding'. The addition is usually odourless and tasteless, but can be detected chemically or physically. The control of vodka purification with activated charcoal has been discussed by a number of authors.⁷⁻⁹ Maravin¹⁰ showed that the chemical action of activated charcoal on alcohol is to produce the ethyl esters of a number of fatty acids, if the latter are present in the alcohol before treatment. Košťál¹¹ discussed Russian vodka from the standpoint of comparison of the alcohol and the quality of the water used. He also gave the analysis of some of the main Russian vodkas and discussed vodka production in Poland and Czechoslovakia.

Experimental

(A) *Analysis of the gin and vodkas*

Gallon samples of vodka (65.5° and 80° proof) and London dry gin were filtered through membrane filters to ensure a bright filtrate. Samples of each were analysed for alcohol, potassium, sodium, calcium, magnesium, iron, copper, and pH by the methods previously described.¹² They were also analysed for alkalinity : a few drops of phenolphthalein were added to a 100-ml. sample and titrated to pH 8.3 (pH meter) with 0.02N-hydrochloric acid. Methyl orange was added and the titration continued to pH 4.5.

(B) *Analysis of vodka deposit*

The following preliminary and spot tests were performed on the deposit : solubility in water and dil. hydrochloric acid, flame test, CO₂ by baryta water, zinc by ammonium mercuri-thiocyanate and silica by microcosmic salt. By centrifuging, the white deposit (approximately 0.1 ml.) was collected from one bottle. This was dissolved in a few drops of conc. AnalaR hydrochloric acid and made up to 10 ml. with distilled water. The supernatant vodka (100 ml.) was evaporated to dryness and ashed overnight at 600°. The white ash was extracted with a few drops of conc. AnalaR hydrochloric acid and water and made up to 10 ml. and both solutions were quantitatively examined for calcium.

(C) *Addition experiments to gin and vodka*

Samples were inspected daily for the first 4 weeks, then weekly for the next 2 months and then monthly. A control using fusel-free alcohol was carried out for each experiment.

(a) *Cationic additions*.—To 50-ml. samples of vodka, at 65.5° and 80° proof, were added sufficient aqueous solutions of the following to increase the cation concentration by 5 or 10 p.p.m.: AnalaR-grade ammonium acetate, aluminium sulphate, cupric sulphate and acetate, ferrous sulphate, magnesium acetate, sodium acetate, zinc sulphate and standard laboratory grade calcium acetate, ferric chloride, lithium chloride, stannous chloride and zinc acetate. To 50-ml. samples of gin were added sufficient aqueous solution of AnalaR-grade copper acetate, ferrous sulphate and zinc acetate to increase the cation concentration by 1 or 5 p.p.m. and the acetates of calcium and magnesium to increase the cation concentration by 5, 10, 15, 20, 25 and 30 p.p.m.

(b) *Anionic additions*.—A similar experiment to C (a) was carried out with AnalaR sodium carbonate, chloride, nitrate and sulphate and potassium dihydrogen phosphate to increase the anion concentration by 10 p.p.m.

(c) *Metal additions*.—In 50-ml. samples of both vodkas and the gin was placed a piece of metal approximately 1 sq. cm. surface area. The metals used were aluminium, brass, copper, lead and zinc.

(D) *Determination of critical solubilities in vodka and gin*

(a) *Solubility of calcium carbonate in spirit, vodka and gin*.—Each spirit (150 ml.) was placed in a stoppered flask with excess of calcium carbonate and left in a thermostatic bath at 20° for 3 days with periodical agitation. They were quickly passed through a membrane-filter and the pH determined. The filtrate (25 ml.) was evaporated to dryness in a silica crucible and the residue dissolved in a few drops of conc. AnalaR hydrochloric acid and water, and the solution titrated for calcium with EDTA.

(b) *Saturation of vodka with calcium carbonate*.—Bottles of vodka were shaken up at room temperature with excess of calcium carbonate and membrane-filtered. The filtrates were bottled and laid down so that the time for the onset of deposition could be observed. The filtrates were then analysed for calcium, sodium and alkalinity.

(c) *Comparison of waters*.—Samples of London mains, softened, demineralised and Edinburgh town waters were analysed over 6 months and the results for calcium, alkalinity and sodium averaged.

Results

The analysis of the spirits is shown in Table I. Analysis of the white deposit formed in vodka showed it to be calcium carbonate, with no zinc or silica present. The cationic additions produced the same results with both vodkas, i.e., aluminium ions, white deposit, copper as acetate or sulphate light blue deposit, iron (II and III) brown deposit, zinc as acetate or sulphate white deposit, all after 3 days. Gin showed a white deposit with copper ions after 5 days, brown deposit with ferrous ions after 1 day and a slight white deposit with the two largest quantities of magnesium and all the calcium after 6 weeks. The only anion to give a deposit was H_2PO_4^- , which came down as a heavy white deposit after 17 days with both vodkas and gin.

Table I*Analysis of spirits*

	Vodka		Gin
	65.5	80	
Alcohol, ° proof	65.5	80	70
Alcohol, % by volume at 20°	37.5	45.8	40.0
Obscuration	0.7	0.7	nil
Potassium, p.p.m.	1.8	3.2	0.3
Sodium, p.p.m.	72	64	45
Calcium, p.p.m.	1.0	1.0	1.0
Magnesium, p.p.m.	nil	nil	1.7
Iron, p.p.m.	nil	nil	0.1
Copper, p.p.m.	nil	nil	0.4
pH	7.65	7.95	6.82
Alkalinity, mequiv./l.	3.2	3.7	2.6

The action of metals on vodka showed that aluminium gave a slight white deposit after 2 weeks, iron gave rust after 1 week (65.5°) and 1 day (80°), zinc a white deposit after 1 day, but no deposit was produced with brass, copper or lead. Gin gave a slight deposit with brass after 3 months, iron rust after 1 day, lead a slight white deposit after 3 months, zinc a white deposit after 1 day, but no deposit with aluminium or copper. Brass, copper, lead and iron did not give a deposit with the standard (fusel-oil-free alcohol), but aluminium and zinc gave a slight white deposit after 3 months. There was no significance in the pH values for deposition and non-deposition for either cationic or anionic additions. Metal additions produced an increase of 2–3 pH units. Zinc gave the greatest increase in pH to the following values: vodka 65.5° (10.95), 80° (11.22); gin (10.96); and alcohol (9.22).

The solubility experiments showed that calcium carbonate was slightly more soluble in spirit than vodka and gin. The values (p.p.m.) were: at 65.5° proof, spirit 9.1, vodka 7.6; at 80° proof, spirit 7.3, vodka 6.4; at 99.2° proof, spirit 6.5, vodka 3.8; and in gin at 70° proof 2.9 p.p.m.

The effect of saturating vodka with calcium carbonate and the 'reducing' (i.e., diluting) water on deposition is shown in Table II. The results of the saturation with calcium carbonate have been averaged.

Table II

Results with different waters and adding calcium carbonate to vodka

(K values as mequiv. of ion per l.)

Proof	Water	pH	K _{Ca²⁺}	K _{HCO₃⁻}	K _{OH⁻}	K _{Na⁺}	C	C _x	C _y	Remarks
65.5°	Demin.	7.4	0.03	0.28	nil	0.89	—	0.008	0.007	No deposit
65.5°	Demin. + CaCO ₃	7.7	0.065	0.44	nil	0.91	—	0.028	0.025	Deposit 6 weeks
65.5°	Soft	9.75	0.04	2.72	0.38	3.09	0.041	0.108	0.334	Deposit 2 weeks
80°	Demin.	7.7	0.03	0.36	nil	0.82	—	0.011	0.009	No deposit
80°	Demin. + CaCO ₃	7.7	0.06	0.38	nil	0.78	—	0.023	0.018	Deposit 6 weeks
80°	Soft	9.5	0.03	2.16	0.30	2.91	0.019	0.065	0.189	Deposit 6 weeks

Demin. = demineralised

A comparison of waters available for vodka production and use for 'reducing' purposes is given in Table III.

Table III

Comparison of various waters (average results)

	K _{Ca²⁺}	K _{HCO₃⁻}	K _{Na⁺}	C _x	C _y
London tap	5.5	0.952	1.56	5.236	8.1682
London soft	0.04	0.952	3.57	0.038	0.1355
London demineralised	0.04	0.02	0.217	0.0008	0.00017
Edinburgh town	0.35	0.56	0.37	0.196	0.0725

Discussion

The action of some metal ions on vodka and gin differs from that of the metals. Copper salts produced deposits but metallic copper did not affect the spirits apart from increasing their pH values by approximately 2 units. The quicker appearance of a deposit with metals than their salts is due to the greater concentration produced in the spirits. Although there is an increase in pH with the metals, the salts produced only a small increase. Examination of the pH values of all the addition experiments indicated that there is no critical value upon which deposition depends as in the case of whisky, rum and brandy. This is to be expected since there is no maturing period in wood during which wood products would be dissolved.

The deposition of calcium carbonate in vodka is the major problem which occurs as $\text{Ca}(\text{HCO}_3)_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O} + \text{CO}_2$. Zel'tser¹³ showed, from mass action considerations, that CaCO_3 will be precipitated if the product of the concentrations of HCO_3^- , OH^- and Ca^{2+} ions is greater than a constant C . Having determined C and estimated HCO_3^- and OH^- then the maximum value of Ca^{2+} can be determined:

$$K_{\text{Ca}^{2+}} \leq \frac{C}{K_{\text{HCO}_3^-} \cdot K_{\text{OH}^-}}$$

where K = concentration in mequiv./litre.

He evaluated C by adding calculated quantities of calcium bicarbonate to 40% aqueous alcohol and analysing the filtrate before and after storage. He obtained $K_{\text{Ca}^{2+}} = K_{\text{HCO}_3^-} = K_{\text{OH}^-} = 0.91$ mequiv./l., giving C a value of $0.91^3 = 0.75$. In present experiments the hydroxide alkalinity was always nil when demineralised water was used and a new constant $C_x = K_{\text{Ca}^{2+}} \cdot K_{\text{HCO}_3^-}$ was introduced. The influence of other ions in solution is to decrease the solubility of the carbonate. When softened water is used, the sodium content is comparatively high especially if the original water is very hard. The product $C_x \cdot K_{\text{Na}^+}$ was called C_y , but examination of Zel'tser's results and the present ones did not show any significance in the values of the product and deposition, but the concentration of other ions should be kept as low as possible. Knowing the critical value for C_x it is possible to calculate the limits of a critical value for the processing or reducing waters. From the present results it was found that the limits of C_x to avoid deposition were at 65.5° proof < 0.028 and 80° proof < 0.023 . Consequently to avoid deposition, only demineralised water can be used. The calculated Russian values at approximately the same strengths were, at 70° proof < 0.828 and 87° proof < 1.447 . The present lower C_x values are probably due to the additions made after processing and the fact that the deposition found is only slight and that no turbidity was found as reported by Zel'tser. The deposit found appeared at the interface between the liquid, glass and vapour rather than settling in the bottom of the bottle.

Other salts which can cause deposition in 40% vodka are magnesium carbonate and calcium and magnesium sulphate. They were given critical values C_1 , Z and Z_1 thus.

$$\begin{array}{r} K_{\text{Mg}^{2+}} \cdot K_{\text{HCO}_3^-} \cdot K_{\text{OH}^-} \\ K_{\text{Ca}^{2+}} \cdot K_{\text{SO}_4^{2-}} \\ K_{\text{Mg}^{2+}} \cdot K_{\text{SO}_4^{2-}} \end{array} \quad \begin{array}{l} C_1 = 244 \\ Z = 0.44 \\ Z_1 = 1.09 \end{array}$$

The sulphate content of untreated and softened water is approximately 82 p.p.m. as SO_4^{2-} which gives a $K_{\text{SO}_4^{2-}}$ value of 1.7. Softened water has its calcium content easily reduced to 2 p.p.m. which is $K_{\text{Ca}^{2+}} = 0.1$, hence $Z = 0.17$. The formation of magnesium carbonate or sulphate should not be troublesome since it is unlikely that the magnesium content in softened water is greater than 1 or 2 p.p.m. Various authors¹⁴⁻¹⁷ have discussed the hardness due to calcium and magnesium and methods of softening the waters used. The use of demineralised water is strongly recommended, where possible, for processing and reducing vodka. If this is not possible, then solubility experiments should be carried out to determine the concentrations of ions a particular vodka will retain without deposition. From the results obtained, calculations can be made for their permissible limits in the water to be used.

Conclusions

It is concluded that for good quality gin and vodka a 'clean' spirit must be used. The deposition of calcium carbonate in vodka does not depend on a critical pH as do the deposits in other potable spirits. The final concentration of ions in the vodka, which can combine to form an insoluble compound, is critical. This value will depend upon whether any deposition is acceptable or not. There is no danger of pick-up of ions from filter-pads, since the vodka will be only slightly acid if made with demineralised water and slightly alkaline if made with softened water. The standard of the water used throughout is the most important factor in preventing deposition. Gin and vodka should not be allowed to come into contact with zinc, iron or aluminium unless the surface of the metal is protected.

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ISOFLAVONE CONTENTS OF RED AND SUBTERRANEAN CLOVERS

By E. WONG

The concentrations of the isoflavones biochanin A, genistein, formononetin, pratensein and daidzein in leaves of four varieties of red clover and two of subterranean clover have been measured by a paper chromatographic-spectrophotometric method.

Biochanin A and formononetin are the predominant isoflavones in red clovers whereas biochanin A and genistein are the most abundant in subterranean clovers. For both species the isoflavone levels differed between varieties and between sampling dates. Higher levels were found during flowering for red clovers and before flowering for subterranean clovers.

The isoflavone contents have been calculated to have oestrogenic activity equivalent to 2-17 μ g. of stilboestrol (% dry wt.) for the red clover samples and 22-48 μ g. of stilboestrol (% dry wt.) for the subterranean clover samples. The potency of some of these samples is much higher than potencies previously reported in the literature.

Introduction

Many biological studies have been made on the oestrogenic activity of subterranean clover (*Trifolium subterraneum*) and red clover (*Trifolium pratense*) in various parts of the world.¹⁻⁴ Bioassay methods as used in these studies detect only the total activity of the plant material ; detailed analysis of the active principles by chemical methods has so far received little attention.

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