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THE FLAVOUR CONSTITUENTS OF GIN

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SUMMARY

London Dry Gin is distilled from ethanol and botanical ingredients which impart the characteristic flavour. The direct analysis of gin by gas chromatography is shown to provide very limited information. On the other hand, continuous extraction with Freon 11 is found to yield representative flavour concentrates, suitable for analysis by gas chromatography–mass spectrometry. The principal flavour volatiles are identified.

INTRODUCTION

Gin has been produced in one form or another for approximately 300 years. Its origin is credited to a 17th century Dutch professor, Franciscus de la Boë, who first distilled "Essence de Genièvre" from a mixture of fermented rye and juniper berries. Various contractions of the French term, resulted in the English word "gin". The somewhat chequered history of gin has been described elsewhere[1].

Basically, all gins are made by distilling spirit in the presence of a carefully balanced selection of botanical ingredients. The botanical formulation always includes juniper berries and can include several other botanicals drawn from a long list, *e.g.* coriander seeds, calamus root, cardamom seeds, cinnamon bark, angelica root, etc. All of these materials contain essential oils which are largely responsible for the flavour of most gins.

Although there are several variations on the basic theme, the two most common types of gin are London Dry Gin (LDG) and Dutch Gin (Geneva).

Dutch gin resembles the original gin produced in the 17th century, in that its flavour, reminiscent of almonds, is derived from the botanical ingredients *and* the source of the spirit used to make it. The raw materials which are fermented, are malted barley and maize or rye, and the resultant liquid (wort) is distilled twice in pot stills to recover a "malt-wine". This is then redistilled with juniper berries and other botanicals to produce Geneva, which is heavily flavoured.

London Dry Gin is the most famous and popular gin to-day. The description

"London" relates to the method of production and not to the geographical location of the distillery; "Dry" means that the flavour level is low. It is produced by re-distillation of neutral spirit in the presence of various botanicals, rich in essential oils. Juniper berries form the basis of any gin formulation and coriander seeds are also used frequently. The ratio of volume of spirit to weight of botanicals determines the overall flavour level of the distilled gin[2].

This paper is concerned with the development of methods for the analysis of the flavour volatiles present in London Dry Gin.

EXPERIMENTAL

Gas chromatographic analysis of gin/gin extracts

Conditions were as follows. (1) Instrument, Pye 104/64 chromatograph; column, 9 ft. × 1/4 in., 15% Carbowax 20M on Chromosorb W AW DMCS (80–100 mesh); nitrogen carrier gas at a flow-rate of 40 ml/min; temperature, 70–220° at 3°/min; detector, 250°; chart speed, 10 in./h. (2) Column, 100 m × 0.01 in. I.D., coated capillary column (Carbowax 20M); instrument, Varian 1840 series chromatograph with Matrix Temperature programmer.

Mass spectrometry

(1) Instrument, Pye 104/64 chromatograph coupled to AEI MS 30 mass spectrometer; column, 9 ft. × 1/4 in., 15% Carbowax 20M; temperature, 100 and 140°. (2) a 50-ft. PLOT column (3% Carbowax 20M) temperature programmed from 80–210° at 2°/min; nitrogen flow-rate, 1 ml/min.

Retention data were calculated as Kovats retention index.

RESULTS AND DISCUSSION

Direct analysis of gin

From a quality control standpoint a direct method of analysis is to be preferred. Previous studies[3–7] have dealt exclusively with the determination of ethanol and minor congeners in the neutral spirit. Accordingly it was decided to test the feasibility of direct analysis by the examination of a range of five different gins, using flavour profile testing[8] ultraviolet spectroscopy and gas–liquid chromatography (GLC).

Tasting revealed significant differences in flavour, which are summarised as follows. Sample 1 was predominantly juniper-based with little foreign character derived from the base spirit. It was ranked fairly high in quality. Sample 2 was scored low for total flavour level (in agreement with its subsequent instrumental analysis). The sample contained an atypical flavour assigned to "tails". Samples 3 and 4 were both scored significantly for orange, sample 3 containing the lower level. Sample 4 contained a slightly higher level of "foreign" character, which was described as "aniseed". Sample 5, Geneva gin, is unlike LDG and atypical odours are assigned to the categories "tails" and "foreign character".

UV analysis provides information on botanical flavour levels since juniper oil absorbs between 200 and 240 nm and coriander oil between 200 and 225 nm. Results from the spectra obtained on analysis of the five samples are given in Table I. The

TABLE I

UV ANALYSIS OF GIN SAMPLES

1-cm cell; 40% ethanol reference.

Sample	*Dilution*	*ppm Juniper*	*ppm Coriander*	*ppm Cassia*
1 London Dry Gin	1:1	45.8	18.1	—
2 London Dry Gin containing cassia	1:1	27.7	6.7	0.5
3 London Dry Gin containing orange	1:1	37.5	19.6	—
4 Plymouth Gin	1:1	37.5	24.6	—
5 Geneva Gin	5:1	87.6	26.2	—

results show that the concentration of juniper oil in commercial gin samples varies from 25 to 50 ppm and for coriander oil from 5 to 25 ppm. The results obtained for Geneva gin (sample 5) must be regarded with caution since this product contains other species such as aldehydes, esters, etc. formed during fermentation. The spectrum showed an absorption at 277 nm which was assigned to furfural. Sample 2 showed an absorbance at 289 nm which was assigned to cinnamaldehyde; this compound is normally derived from either cassia bark or cinnamon bark. UV cannot differentiate between gin containing orange oil and those not containing this botanical, since limonene, the principal component, absorbs at 200 nm coincident with the absorption of coriander oil.

UV analysis only provides an indication of "total flavour level" as "Juniper" or "Coriander". This is because the oils used for standardisation are steam distilled products, whereas gin is distilled in ethanol and part of the botanical flavour components are rejected as "feints".

The gin samples were also examined by gas chromatography using Carbowax 20M columns. The chromatograms are shown in Fig. 1 and the quantitative results are summarised in Table II.

When these results are linked to odour threshold values and the conclusions of the taste panel, some interesting observations can be made (see Table II):

(1) The odour threshold of steam distilled coriander oil is 0.7 ppm (ref. 9). Since the odour threshold of linalool (the major component of coriander oil) is 9 ppm, this compound is not responsible for the orangey/spicey character of the oil. γ-Terpinene has an odour threshold of 1.5 ppm and also possesses an orangey aroma. This contributes significantly to coriander aroma.

(2) The odour threshold of juniper oil is 2.0 ppm (ref. 9). This indicates that *p*-terpinenol is not a principal odour component, since its threshold value is 13 ppm. α-Pinene is masked by the ethanol peak in all the analyses illustrated, but most gins contain α-pinene at approximately 5 ppm (ref. 9). Since its odour threshold is 2 ppm, this monoterpene must contribute significantly to overall aroma.

(3) The odour threshold of limonene (6.5 ppm) is in good agreement with results obtained in the flavour profile tasting. Gins described as "orangey" and scored relatively high for "orange" character contain limonene at levels above its threshold, *e.g.*, Gin 1: limonene content 2.5 ppm, score for "orange", 1.0; Gin 3: limonene content, 14 ppm, score for "orange", 2.9; Gin 4: limonene content, 18 ppm, score for "orange", 3.9.

(4) The threshold of cinnamaldehyde (3 ppm) is fairly high, and this level is

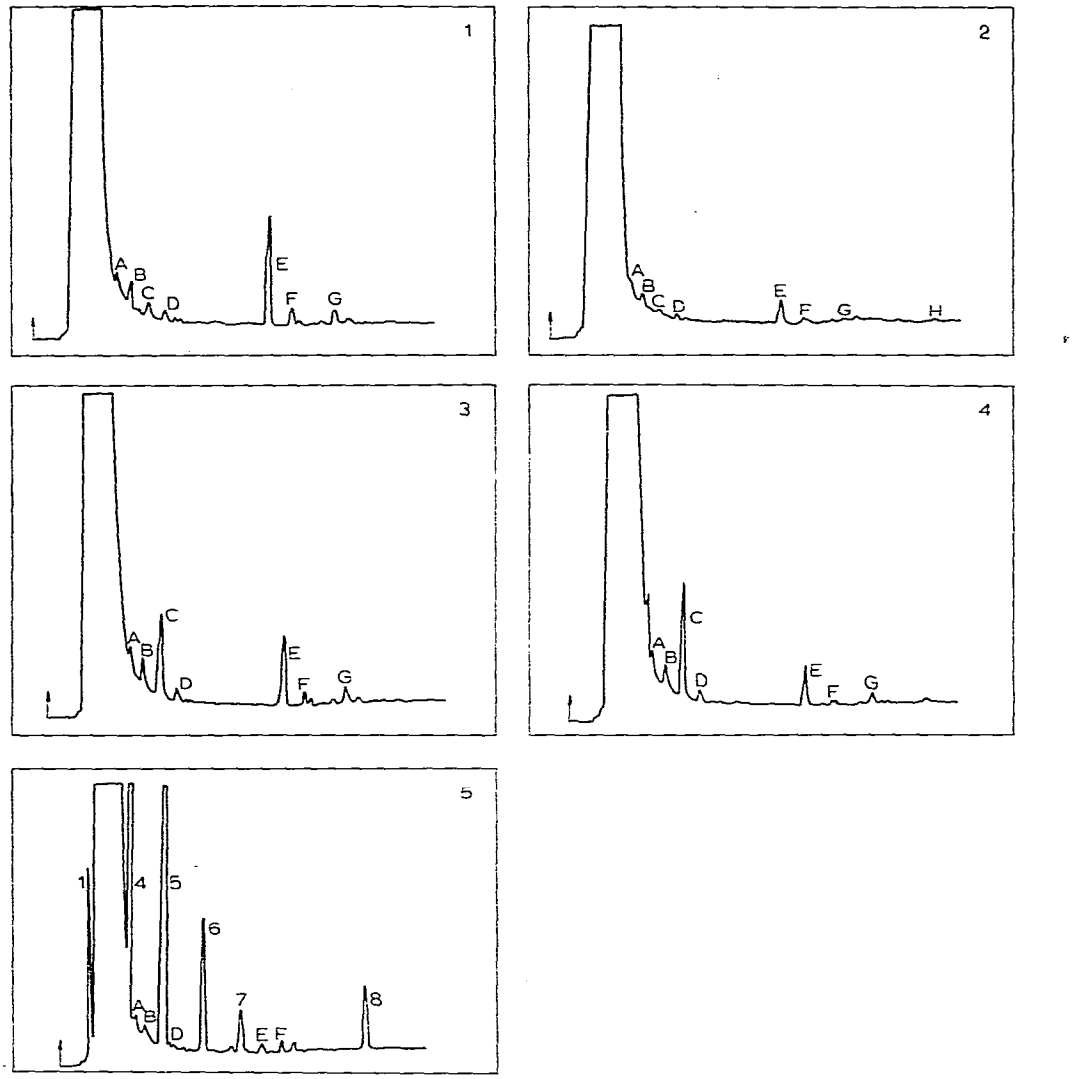

Fig. 1. Direct GLC analysis of five different London Dry Gin samples. For detail see text. Column, 9 ft. × 1/4 in., 15% Carbowax 20M.

not attained in normal gins containing cassia or cinnamon, *e.g.*, Gin 2 contains 0.5 ppm cinnamaldehyde.

(5) Geneva gin contains higher alcohols at similar levels to those found in Scotch whisky, but only isoamyl alcohol exerts any significant effect on flavour.

Although direct gas chromatography of gin yields some useful information, it is apparent that the method lacks the sensitivity necessary to reveal all the compounds that contribute to the overall flavour. Accordingly, it was decided to attempt to concentrate the gin flavour using extraction techniques.

TABLE II

QUANTITATIVE ANALYSIS OF GIN SAMPLES BY GLC

Gins analysed using 9 ft. × 1/4 in. 15% Carbowax 20M columns, programmed from 70° to 220° at 3°/min.

Component	*Odour threshold (ppm) in 20% ethanol*	*Concentration (ppm) of components*					
		Gin 1	*Gin 2*	*Gin 3*	*Gin 4*	*Gin 5 Geneva*	*Blended Scotch whisky*
A β-Pinene	3.5	1.0	0.2	0.5	0.4	0.7	–
B Myrcene	1.0	4.5*	1.2*	4.5*	3.8*	2.0*	–
C Limonene	6.5	2.5	0.6	14.0*	18.0*	–**	–
D γ-Terpinene	1.5	1.5*	0.5	1.5*	1.5*	0.3	–
E Linalool	9.0	16.0*	3.5	11.0*	6.3	2.0	–
F p-Terpinenol	13.0	3.0	0.7	2.5	0.7	2.2	–
G Unidentified sesquiterpene		2.8	0.4	3.0	2.5	–	–
H Cinnamaldehyde	3.0	–	0.5	–	–	–	–
1 Ethyl acetate	50.0	–	–	–	–	26.1	97.6*
2 2-Butanol	35.0	–	–	–	–	5.3	–
3 Propanol	2800	–	–	–	–	91.4	137.0
4 Isobutanol	240	–	–	–	–	73.0	279.0*
5 Isoamyl alcohol	6.0	–	–	–	–	317.0*	313.0*
6 Hexanol	17.0	–	–	–	–	9.5	1.4
7 Furfural	20.4	–	–	–	–	5.3.	1.2
8 β-Phenyl ethanol	26.2	–	–	–	–	9.4	3.1

* At or above threshold limit.

** Interference from isoamyl alcohol on Carbowax 20M.

Isolation of the flavour volatiles of gin

Descriptions of the extraction of the flavour constituents of foodstuffs and alcoholic beverages are legion. In general two techniques are used, namely liquid–liquid extraction[10–17] and adsorption–desorption[18–22], both of which have their limitations. Accordingly, we have evaluated both methods using a model system, termed "syn-gin", with the following composition: 5 ppm *d*-limonene; 5 ppm *p*-cymene; 20 ppm *d*-linalool; 10 ppm *p*-terpinenol; 10 ppm α-terpineol; 10 ppm geranyl acetate in 40% (v/v) ethanol. The efficiency of the extraction methods were determined by quantitative GLC using cyclohexanone as internal standard.

Liquid–liquid extraction. Solvents are never totally selective towards every class of flavour component, and the optimum system must be chosen as a compromise between percentage recovery and the organoleptic quality of the reconstituted extract. The latter aspect is far too often ignored in many analytical studies on food flavours. Ideally, the solvent used for alcoholic beverages should possess all of the following characteristics: (a) low affinity for ethanol; (b) remain selective towards all flavour compounds; (c) be easily available from commercial sources at an economic price; (d) be available in a reasonable pure, stable state; (e) have reasonably low boiling point; (f) be inert towards flavour components and ethanol–water; (g) have density different from that of 40% ethanol (0.9496 kg/m^3) and (h) be immiscible with 40% ethanol.

A range of solvents was chosen having established these requirements. All solvents were purified by distillation before use. Preliminary screening of the solvents

was carried out using an orbital shaker (100 ml syn-gin, 50-ml solvent) for a nominal period of 17 h. Results (Table III) showed that the three most favourable solvents were: dichloromethane (DCM); trichlorotrifluoroethane ($FCl_2C–CClF_2$), Freon TF113, DuPont; DCM–TF113 (1:1) azeotrope.

TABLE III

SOLVENT EXTRACTION OF SYN-GIN—PERCENTAGE RECOVERIES

100 ml syn-gin + 50 ml solvent; shaker extraction for 17 h.

Solvent	*Limonene*	*p-Cymene*	*Linalool*	*p-Terpinenol*	*α-Terpineol*	*Geranyl acetate*
Carbon tetrachloride	26	24	14	19	20	21
Petroleum ether	31	27	54	41	40	26
Isopentane	31	28	76	39	30	24
Pentane	30	28	74	36	33	30
Diethyl ether–pentane (2:1)	53	56	60	59	59	63
Diethyl ether	37	53	72	59	49	74
DCM	82	90	100	100	100	100
Freon TF113	72	83	77	90	80	80
DCM–TF113 (1:1)	68	57	87	97	98	100

DCM and ethanol form an azeotrope, which contains more than 95% DCM, but this slight solubility was acceptable in the present study. "Salting-out"[23] using a range of 14 different selected salts, added as solutions did not improve the recovery of flavour components from syn-gin; dilution of samples[16,24] also did not improve recoveries, 40% ethanol being the most suitable alcoholic strength; variation of extraction time showed that shaker extraction was reproducible after a period of 5 h.

Fluorocarbon solvents are manufactured under various trade names as refrigerants and degreasing agents. They are virtually insoluble in 40% ethanol. Several previous applications of fluorocarbons for the extraction of various food volatiles have been reported[25–27]. In this present study, TF113 and DCM–TF113 were evaluated using the shaker method; trichlorofluoromethane (Freon 11) was subsequently examined by continuous extraction only due to its high volatility.

The optimum alcoholic strength for shaker extraction of syn-gin using TF113 was found to be 24% ethanol, which is significantly different to the result found with DCM. The optimum for DCM–TF113 mixture was found to be 40% (v/v) ethanol.

The shaker method was found to be very useful and eminently suitable for obtaining a concentration factor of about 20 times. Recoveries for terpene hydrocarbons in syn-gin were around 80%, and 100% for oxygenated compounds.

Continuous extraction methods were also evaluated, in order to obtain a higher concentration factor. Large scale continuous extraction of 750 ml of syn-gin, with DCM was not feasible due to the large volume of the final extract (*ca.* 50 ml); also percentage recoveries were low (Table IV). TF113 gave a final volume of *ca.* 1 ml, but recoveries at 24% (v/v) ethanol were not sufficiently high. The DCM–TF113 mixture gave better recoveries and a final extract volume of 5 ml.

Continuous extraction using Freon 11 required a modification to standard

TABLE IV

CONTINUOUS EXTRACTION OF SYN-GIN

Solvent	*Ethanol (%, v/v)*	*Recovery (%)*					
		Limonene	*p-Cymene*	*Linalool*	*p-Terpinenol*	*α-Terpineol*	*Geranyl acetate*
DCM	40	31	27	49	51	47	39
TF113	24	46	57	76	92	96	85
TF113	40	67	70	67	85	76	75
DCM–TF113	24	54	88	95	98	100	100
Freon 11	24	32	39	53	62	72	78
Freon 11	40	73	75	89	98	101	96

equipment[28]. The apparatus* is specifically constructed to accommodate 750 ml sample at 40% ethanol, and 100 ml of Freon 11. The Freon is poured into the base of the extractor and the alcohol sample added. The sinter, when positioned, displaces approximately 50 ml of Freon into the flask to provide sufficient for refluxing. All extractions are carried out in a fume cupboard and circulation of water at 8° is necessary through the condenser and around the extractor base. Extractions are reproducible after 22–24 h.

The recoveries at 40% (v/v) ethanol were higher than at 24% (v/v) ethanol. The volume of extract after solvent removal is approximately 0.5 ml which represents a concentration factor of 1500×. The extract is suitable for detailed analysis, and is well suited for normal gin samples bottled at 40% (v/v) ethanol.

Application to commercial gin samples

Since the experiments with model systems revealed that the best methods were shaker extraction with DCM and continuous extraction using Freon 11, these techniques were then applied to commercial samples of gin. The extracts obtained were analysed by GLC. The chromatograms obtained, typical examples of which are shown in Fig. 2, clearly demonstrate that continuous extraction yields superior results in that much less ethanol is co-extracted.

Reconstitution of the extracts obtained using Freon 11 showed that they were virtually identical organoleptically to the original samples. Tasting using the triangular test showed no significant difference between original and reconstituted samples.

Therefore it is recommended that continuous extraction with Freon should be used for the quantitative analysis of the flavour volatiles of gin. Subsequent studies have shown that the method is equally applicable to other spirits including brandy, rum and whisky.

An adsorption method using charcoal columns was also evaluated but the extracts were found to be organoleptically inferior to those obtained by continuous liquid extraction. The charcoal extract, however, is suitable for detailed analysis using capillary columns (Fig. 2D).

* Copies of diagram of apparatus available from author.

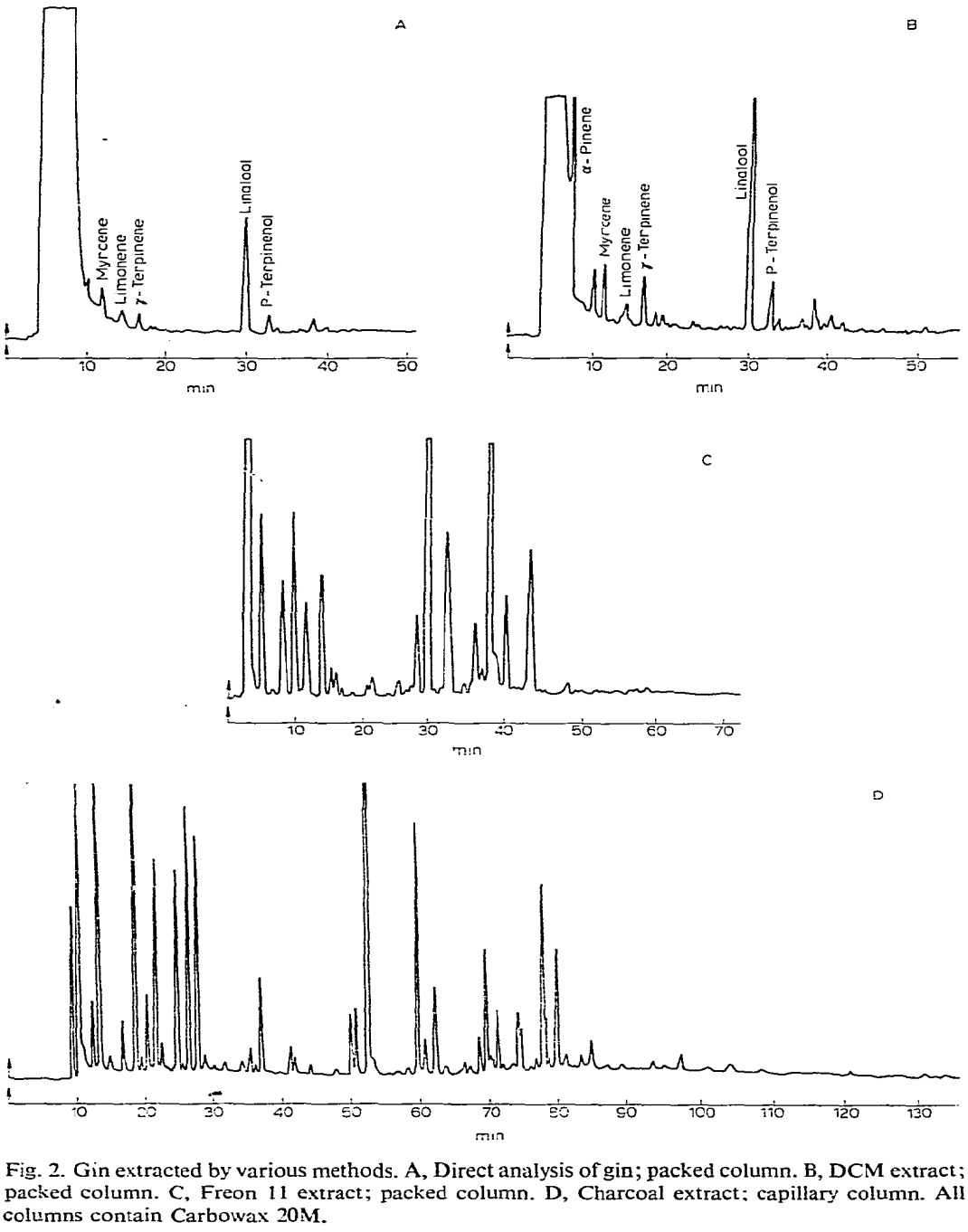

Fig. 2. Gin extracted by various methods. A, Direct analysis of gin; packed column. B, DCM extract; packed column. C, Freon 11 extract; packed column. D, Charcoal extract; capillary column. All columns contain Carbowax 20M.

Analysis of gin extracts

Analysis of gin extracts obtained by Freon extraction (Fig. 3), were undertaken to compare the flavour components with those present in the steam-distilled essential oils of juniper berries and coriander seeds[29]. Analysis by GC–mass spectrometry (MS) confirmed that all of the major components originated from the juniper and coriander oils (see Table V). Several minor artifacts (*in Fig. 3) were formed during the extraction process, but these could not be characterised by MS. These components were not present in steam distilled juniper and coriander oils and the distillation process (in copper stills) did not produce any of these substances. Organoleptic evaluation of the extract showed that these artifacts exerted no significant effect on odour quality.

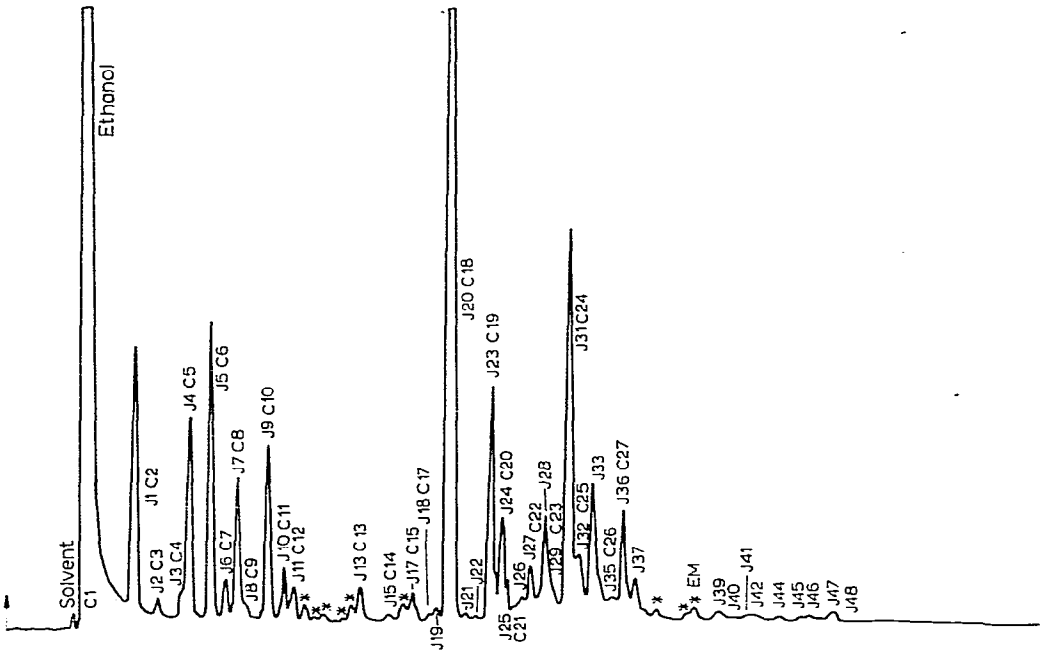

Fig. 3. Freon 11 extract of commercial gin sample showing origin of principal components J = juniper, C = coriander, * = artifact formed during extraction.

Variations in flavour composition during gin distillation

GLC analysis of fractions obtained from a production scale gin distillation produces some valuable information. The "foreshot" (heads) contains large quantities of monoterpene hydrocarbons from both juniper and coriander and a small amount of higher boiling sesquiterpenes (J41–J47, Fig. 3). Their presence in foreshot results from the previous gin distillation where these components are adsorbed on the inside surface of the still neck, lyne arm, and condenser.

As the distillation proceeds, the concentration of monoterpenes decreases reaching a minimum at an alcoholic strength of approximately 80% (v/v) ethanol. Linalool, the principal constituent of coriander, reaches a maximum at approximately

TABLE V

COMPOUNDS IDENTIFIED IN EXTRACT OF LONDON DRY GIN

× × = Absolute confirmation by this technique, × = tentative confirmation by this technique. J = present in juniper berry oil, C = present in coriander seed oil.

Component	*Identification*	*Basis for identification*	
		MS	*Retention data*
C1	Tricyclene	× ×	—
J1, C2	α-Thujene; α-pinene	× ×	× ×
C3, J2	Camphene	× ×	× ×
J3, C4	β-Pinene	× ×	× ×
J4, C5	Sabinene	× ×	× ×
J5, C6	Myrcene; 3-carene; α-phellandrene	× ×	× ×
J6, C7	α-Terpinene	× ×	× ×
J7, C8	(+)-Limonene	× ×	× ×
J8, C9	β-Phellandrene; 1,8-cineole	× ×	× ×
J9, C10	γ-Terpinene	× ×	× ×
J10, C11	p-Cymene	× ×	× ×
J11, C12	Terpinolene	× ×	× ×
J13, C13	MW 134	×	—
J15, C14	α-Dimethyl styrene; *trans*-linalool oxide; nonanal	×	—
J17, C15	α-Cubebene; *cis*-linalool oxide	×	—
J18, C17	α-Copaene; decanal	×	× ×
J19 .	Camphor + sesquiterpene	×	× ×
J20, C18	Sesquiterpene; linalool	× ×	× ×
J21	Linalyl acetate or 4-terpinenyl acetate	×	—
J22	Bornyl acetate + sesquiterpene	×	× ×
J23, C19	Terpinen-4-ol	× ×	× ×
J24, C20	β-Caryophyllene	× ×	× ×
J25, C21	Sesquiterpene; *trans*-2-decenal	×	—
J26	β-Farnesene	×	—
J27	Monoterpene alcohol + sesquiterpene	×	—
C22	α-Terpineol	× ×	× ×
J28	α-Humulene	× ×	×
C23, J29	Borneol	× ×	× ×
J31, C24	γ-Muurolene; citronellol	× ×	× ×
J32, C25	α-Muurolene; geranyl acetate	× ×	× ×
J33	δ-Cadinene	× ×	—
C26	Nerol	× ×	× ×
J35	γ-Cadinene	×	—
J36, C27	Geraniol	×	× ×
J37	p-Cymen-8-ol; sesquiterpene	×	—
EM	Ethyl myristate	× ×	× ×
J39	α-Copaene epoxide	×	—
J40	Sesquiterpene alcohol (MW 220)	×	—
J41	Sesquiterpene alcohol (MW 220)	×	—
J42	Sesquiterpene alcohol + abietriene	×	—
J44	Sesquiterpene alcohol (MW 220)	×	—
J45	δ-Cadinol	×	—
J46	Sesquiterpene alcohol + diterpene	×	—
J47	Sesquiterpene alcohol (MW 222)	×	—
J48	Diterpene (MW 272)		

70% (v/v) ethanol as the alcoholic strength decreases with time. γ-Muurolene, the principal sesquiterpene constituent of ethanolic juniper distillates, reaches a maximum at approximately 80% (v/v) ethanol and this is easily substantiated by flavour profile tasting.

Although the boiling point of terpinen-4-ol is some 60° lower than that of γ-muurolene, terpinen-4-ol is not present in significant quantity until γ-muurolene has reached its maximum concentration. This is due to differences in relative volatilities and affinity for the aqueous phase.

GLC analysis shows that the early fractions of gin distillates are principally composed of juniper components. Coriander components distill over after a strength of approximately 75% ethanol is reached. Indeed a large quantity of flavouring components are run to waste in many typical distillations.

Analysis of a wide range of gin samples has shown that, as a general rule, a good quality gin should contain γ-muurolene at a level approximately equal to that of *p*-terpinenol. Where *p*-terpinenol predominates, quality is normally poor.

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REFERENCES

1 D. W. Clutton, *Flavour Ind.*, 9 (1972) 454.
2 A. C. Simpson, *Proc. Biochem.*, 10 (1966) 355.
3 R. B. Carrol. *Quart. J. Stud. Alc. Suppl.*, 5 (1970) 6.
4 E. Dorchies, *Ann. Fals. Expert. Chim.*, 28 (1935) 452.
5 M. G. Maticorena, *Ann. Fac. Farm. Bioquim. (San Marcos)*, 4 (1953) 99.
6 H. G. Fernandes, *Rev. Brasil. Quim.*, 42 (1956) 256.
7 A. C. Arias, *An. Real Acad. Farm.*, 32 (1966) 542.
8 M. P. Dixon, *Flavour Ind.*, 1 (1970) 45.
9 International Distillers and Vintners Ltd., Unpublished results.
10 C. Weurman, *J. Agr. Food Chem.*, 17 (1969) 370.
11 M. Potterat and R. Gygi, *Z. Anal. Chem.*, 221 (1966) 312.
12 H. Suomalainen, *Wallerstein Lab. Commun.*, 31 (1968) 5.
13 L. Nykanen, *Tek. Kem. Aikak.*, 20 (1963) 19.
14 L. Nykanen, *Suom. Kemistilehti*, 37B (1964) 230.
15 L. Nykanen, *J. Inst. Brew. (London)*, 72 (1966) 469.
16 H. Maarse, *J. Food Sci.*, 31 (1966) 951.
17 F. Drawert, *Chromatographia*, 1 (1968) 446.
18 N. Paillard, *Fruits*, 20 (1965) 189.
19 F. Drawert, *Chromatographia*, 2 (1969) 57.
20 J. F. Carson, *J. Agr. Food Chem.*, 9 (1961) 140.
21 D. E. Heinz, *J. Food Sci.*, 31 (1966) 63.
22 R. E. Naipawer, *Flavour Ind.*, 8 (1971) 465.
23 J. Boidron, *Ind. Aliment. Agr.*, 84 (1967) 883.
24 H. Suomalainen, *J. Food Sci.*, 33 (1968) 88.
25 T. H. Schultz, *J. Food Sci.*, 32 (1967) 279.
26 P. J. Hardy, *J. Agr. Food Chem.*, 17 (1969) 656.
27 K. L. Stevens, *J. Agr. Food Chem.*, 17 (1969) 1102.
28 D. W. Clutton, *Ph.D. Thesis*, 1976.
29 D. W. Clutton and M. B. Evans, to be published.