Ann. Technol. agric., 1975, 24 (3-4), 239-245.

LESS VOLATILE ALCOHOLS, ESTERS AND HYDROCARBONS IN A RAW AUSTRALIAN RUM

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SUMMARY

A novel source of appreciable amounts of the volatile compounds in rum is described. Examination of the concentrate so produced permitted the positive identification of a number of organic compounds, including 1,1,6-trimethyl-1,2-dihydronaphthalene, heptan-1-ol, heptan-2-ol, 3-methylpentan-1-ol, (—) oct-1-en-3-ol, methyl salicylate and a number of fatty acid esters. The work was carried out on raw rum, *i. e.* rum before maturation. Some of the compounds identified were previously considered to be formed during maturation.

INTRODUCTION

Maarse and Ten Noever (1966) ; Liebich, Koenig, Bayer (1970) extracted mature Jamaican rums with pentane-ether and analysed the extracts using gas chromatography-mass spectrometry and infra red spectrometry. The latter workers identified over 200 compounds. Since a g.c.-m.s. system was not available to the author for the work, the pentane-ether extracts even of many gallons of raw rum (rum that had not yet been matured in wooden vats for 2 years) were too small to allow individual compounds to be easily isolated and identified using infra red, ultra violet and proton magnetic resonance spectroscopy and by making derivatives. Consideration of the industrial process used in the Bundaberg distillery suggested an alternative method of producing concentrates for analysis.

EXAMINATION OF THE INDUSTRIAL PROCESS

Fermentation of molasses forms the starting point for the production of both Bundaberg rum and industrial alcohol. The yeast and fermentation conditions were chosen to suit the production of rum, the alcohol is only a by-product. The compounds present in rum which are absent from industrial alcohol must be removed from the alcohol still in the side streams. Distillery oil, removed in litre quantities from the side of the still was shown to contain these compounds and can be considered as a concentrate of higher boiling point flavour compounds of rum. This was confirmed by showing that gas chromatograms of distillery oil and pentane-ether extracts of raw rum were identical.

Fractional distillation of distillery oil produced « fusel oil » containing the higher alcohols (*n*-propanol, isobutanol, isoamyl alcohol and active amyl alcohol, BP to 132°C) and a residue termed « rum » oil containing compounds with a higher boiling point than isoamyl alcohol. Only the analysis of the « rum » oil will be discussed.

RESULTS AND DISCUSSIONS

A. — *Distillation and analysis of « rum » oil*

The « rum » oil (500 ml) was distilled in a LECKY and EWELL (1942) still. The fractions that were gas chromatographically impure were redistilled in a BOWER and COOKE (1943) still. Many of the compounds listed in table 1 were then positively identified by IR, PMR spectrometry, by preparation of derivatives and by synthesis.

B. — *Hydrolysis of distillery oil*

Since the major compounds were esters, 1 litre of « rum » oil was prepared and hydrolysed with sodium hydroxide to concentrate the remaining compounds. A gas chromatogram of this hydrolysate on 10 ft Carbowax 20M at 100°C produced sixteen (16) significant peaks (fig. 1). The hydrolysate was fractionally distilled and the fractions analysed. From figure 1, it can be seen that all of the compounds producing peaks are alcohols except for those which comprised peak 16. The major compound in peak 16 was identified by synthesis and analysis in a mass spectrometer as 1,1,6-trimethyl-1,2-dihydronaphthalene. The alcohols with boiling points lower than pentan-1-ol were produced wholly by hydrolysis of esters present in the original distillery oil.

C. — *Other compounds present in « rum » oil*

A group of nitrogen compounds was isolated using the HCl extraction method of WOBBEN (1971), but the volume of the extract was too small to be analysed by conventional means. Although LIEBICH (1970) identified many acetals, none were

identified in the « rum » oil, possibly due to their instability during distillation of the acidic distillery oil to remove the fusel oil. Raw rum contained at least 50 p.p.m. of 1,1-diethoxyethane and this concentration increased in mature rum. As this and other compounds more volatile than isoamyl alcohol did not occur in « rum » oil, they are not listed in table 1.

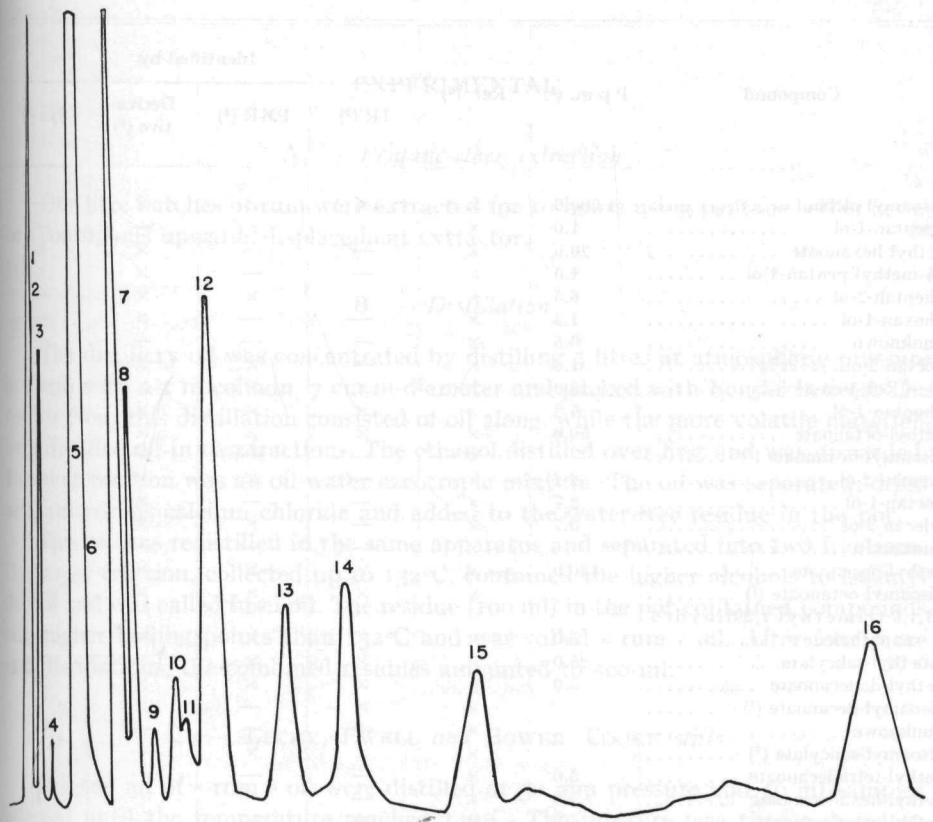


FIG. 1. — *Gas chromatogram of hydrolysed « rum » oil*

Column : 10ft Carbowax 20M ; Temperature : 100°C

1 : Ethanol + methanol
2 : *n*-propanol
3 : Isobutanol
4 : Butan-1-ol
5 : Isoamyl + Active Amyl Alcohols
6 : Pentan-1-ol (*)
7 : Heptan-2-ol
8 : Hexan-1-ol
9 : Unknown Alcohol
10 : Octan-2-ol
11 : Unknown Alcohol
12 : Heptan-1-ol
13 : Nonan-2-ol
14 : Octan-1-ol
15 : Decan-2-ol
16 : 1,1,6-trimethyl-1,2-dihydronaphthalene

D. — *Conclusions*

All of the compounds listed in table 1, other than several of the secondary alcohols, in particular, (—) oct-1-en-3-ol, exist in mature Jamaican rum (LIEBICH, 1970). However, the concentrations of many of the flavour compounds are considerably

(*) Peak clearly visible in original g. c.

TABLE I

Compounds in « rum » oil

Compound	P.p.m. (1)	Ret. (2)	Identified by			
			IR (3)	PMR (4)	Derivative (5)	Syn (6)
isoamyl alcohol	1 000.0	×	×	×	×	—
pentan-1-ol	1.0	×	×	×	—	—
ethyl-hexanoate	20.0	×	—	—	×	×
4-methyl-pentan-1-ol	1.0	×	—	—	×	×
heptan-2-ol	6.5	×	×	×	×	—
hexan-1-ol	1.3	×	—	—	×	—
unknown	0.5	×	—	—	—	—
octan-2-ol	1.0	×	—	×	×	—
(—) oct-1-en-3-ol	15.0	×	×	×	×	×
heptan-1-ol	4.2	×	×	×	×	—
ethyl-octanoate	50.0	×	×	×	×	×
isoamyl hexanoate (7)		×	—	—	—	×
nonan-2-ol	2.2	×	—	×	×	—
octan-1-ol	2.7	×	—	—	×	—
decan-2-ol	3.7	×	—	×	×	—
unknown		×	—	—	—	—
ethyl-decanoate	130.0	×	×	×	×	—
isoamyl-octanoate (7)		×	×	×	×	—
1,1,6-trimethyl-1,2-dihydro-naphthalene	5.0	×	×	×	—	×
methyl-salicylate	25.0	×	×	×	×	×
ethyl-dodecanoate	5.0	×	×	×	×	×
isoamyl-decanoate (7)		×	×	—	×	×
unknown		×	—	—	—	—
isoamyl-salicylate (7)		×	×	×	—	×
ethyl-tetradecanoate	5.0	×	—	—	—	×
ethyl-hexadecanoate	5.0	×	—	—	—	×
ethyl-octadecanoate	5.0	×	—	—	—	×
benzyl-alcohol		×	—	—	—	—
β-phenyl-ethyl-alcohol		×	—	—	—	×

(1) P.p.m. : parts per million parts of rum (68 p. 100) alcohol by volume.
(2) (*i*) Gas chromatographis retention times checked on TCEP, Carbowax 20M, Carbowax 600 and FFAP.
(*ii*) Compounds found by retention time only cannot claim to be positively identified.
(3) Infra red spectrometry.
(4) Proton magnetic resonance spectrometry.
(5) The ester fractions were hydrolysed and a derivative made of the acid.
(6) Synthesized.
(7) Transesterification during distillery oil distillation increased the isoamyl esters concentration.

different from those of Bundaberg rum. In particular, ethyl decanoate, methyl salicylate and 1,1,6-trimethyl-1,2-dihydronaphthalene are much more concentrated in raw Bundaberg rum. It must be noted that gas chromatograms of mature and raw rum extracts of Bundaberg rum are very similar, indicating little change in concentration, but no doubt very significant flavour enhancement during maturation.

EXPERIMENTAL

A. — *Pentane-ether extraction*

One litre batches of rum were extracted for 10 hours using pentane- ether (2 : 1) in a continuous upwards displacement extractor.

B. — *Distillation*

The distillery oil was concentrated by distilling 5 litres at atmospheric pressure in a still with a 1 m column, 7 cm in diameter and packed with Fenske helices. The residue from this distillation consisted of oil alone, while the more volatile materials were distilled off in two fractions. The ethanol distilled over first and was discarded. The next fraction was an oil-water azeotropic mixture. The oil was separated, dried with anhydrous calcium chloride and added to the water-free residue in the pot.

This oil was redistilled in the same apparatus and separated into two fractions. The larger fraction, collected up to 132°C, contained the higher alcohols to isoamyl alcohol and was called fusel oil. The residue (100 ml) in the pot contained compounds with higher boiling points than 132°C and was called « rum » oil. After four more such distillations, the combined residues amounted to 500 ml.

C. — Lecky, Ewell *and* Bower, Cooke *stills*

The 500 ml of « rum » oil were distilled at 50 mm pressure and 10 ml samples collected until the temperature reached 129°C. The pressure was then reduced to 10 mm and more fractions removed until the temperature reached 126°C. Several combined fractions (15-30 ml) were redistilled in the Bower, Cooke (1943) still.

D. — *Oct-1-en-3-ol identification*

I.R. spectrum contained peaks at 3.300, 1.620, 1.440, 970 and 900 cm^{-1}, indicating that the compound was an alcohol with a terminal double bond. The following tests established that the alcohol was (—) oct-1-en-3-ol.

1. Optically active : $[\alpha]_D^{25} = -3.2°$ for 5 p. 100 in chloroform.

2. P.m.r. spectrum contained peaks at 0.85, 1.28, 3.7 and 3.96 p.p.m. due respectively to hydrogen on the terminal methyl group, methylenes, hydroxyl group and the carbon to which the hydroxyl was attached. A series of ten peaks from 4.85 to 6.2 p.p.m. with an intensity of 3 protons was due to the ABX system $-CH=CH_2$.

3. Oxidation by Morton's (1948) active manganese dioxide in hexane produced oct-1-en-3-one.

4. Reduction with Raney nickel catalyst produced 3-octanol which was identified by comparison with an authentic sample of 3-octanol made by the GRIGNARD reaction on *n*-amyl bromide and propanol.

5. Synthesis of oct-1-en-3-ol (MURAHASHI'S alcohol) (1937) by the GRIGNARD synthesis using *n*-amyl bromide and acrolein and using the experimental technique given in Vogel.

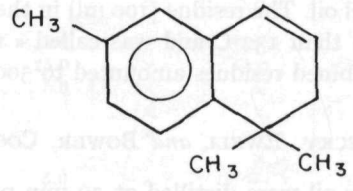
E. — *Hydrolysis of « rum » oil*

The « rum » oil was hydrolysed in 300 ml lots with 500 ml of 20 p. 100 sodium hydroxide. The mixtures were refluxed and stirred with a magnetic stirrer for 48 hours. The compounds formed were extracted into ether.

F. — *1,1,6-trimethyl-1,2-dihydronaphthalene identification*

The ethyl decanoate fraction from the initial distillation of the « rum » oil contained 2 p. 100 of this compound. It was purified by hydrolysis of the ethyl decanoate, steam distillation of the hydrolysate, fractional distillation and purification by absorption on a column of aluminium oxide (activity 2). It was also isolated from hydrolysed « rum » oil.

The u.v. spectral characteristics were $\varepsilon = 9100$, $\lambda_{max} = 261$ cm^{-1}. The i.r. spectrum showed no functional groups. The p.m.r. spectrum gave significant peaks at 1.25 and 2.2 p.p.m. and multiplet peaks at 2.1, 5.4-6.2 and 6.5-7.0 p.p.m. The compound was deduced to be 1,1,6-trimethyl-1,2-dihydronaphthalene.



Synthesis.

1,1,6-trimethyl-1,2-dihydronaphthalene was first produced by TIEMANN (1898) as a minor product during the production of ionene by the condensation of ionone with hydrogen iodide and red phosphorous. BOGERT and FOURMANN (1933) produced ionene by condensing ionene with iodide. This latter method was used and produced 10 p. 100 1,1,6-trimethyl-1,2-dihydronaphthalene and 90 p. 100 ionene as shown by p.m.r. spectral analysis and g.c.-m.s. analysis.

Mass spectral analysis.

A g.c.-m.s. was used to analyse a sample of the compounds in peak 16 (fig. 1). The major compounds was 1,1,6-trimethyl-1,2-dihydronaphthalene with traces of :

a) two isomers of ionene,

b) an aromatic $C_{15}H_{24}$ with molecular ion 204 and a base peak of 189,

c) molecular ion 170, hydrocarbon $C_{21}H_{22}$ reported by Kemp (1971),

d) molecular ion 156, possibly 1,6-dimethylnaphthylene.

ACKNOWLEDGEMENTS

The author wishes to thank the Millaquin Sugar Company for allowing him to publish the data obtained and Professor M. D. SUTHERLAND for supervising the author's Master's thesis of which the results in this paper are a part. He is also indebted to Dr. K. E. MURRAY of the C.S.I.R.O. for the mass spectra.

RÉSUMÉ

ALCOOLS PEU VOLATILS, ESTERS ET HYDROCARBURES DANS UN RHUM BRUT AUSTRALIEN

Une nouvelle source de quantité appréciable de composés volatils du rhum est décrite. L'examen de concentrats ainsi produits a permis l'identification de nombreux composés organiques parmi lesquels : 1-1,-triméthyl-1,2-déhydronaphtalène, heptane-1-ol (—), oct-1-ène-3-ol, méthylsalicylate et de nombreux esters d'acides gras. Le travail a été fait sur du rhum brut, c'est-à-dire avant vieillissement. Quelques-uns des composés identifiés étaient considérés jusqu'ici comme formés pendant le vieillissement.

RESUMEN

ALCOHOLES POCO VOLATILES, ESTERES E HIDROCARBUROS EN UN RON BRUTO AUSTRALIANO

Figura descrita en este artículo una nueva fuente de cantidad apreciable de compuestos volátiles del ron. El examen de concentrados así producidos ha permitido la identificación de un gran número de compuestos orgánicos entre los cuales cabe hacer mención de : 1-1, trimetil-1,2-dehidronaftaleno, heptano-1-1, (—) oct-1 ene-3-ol, metilsalicilato y asimismo, numerosos ésteres de ácidos grasos. El trabajo ha sido efectuado mediante ron bruto, es decir, antes de su añejamiento. Algunos de los compuestos identificados se consideraba que su formación tenía lugar durante el añejamiento.

RIASSUNTO

ALCOOL POCO VOLATILI, ESTERI E IDROCARBURI IN UN RUM GREZZO AUSTRALIANO

Lo studio porta su una nuova fonte di una rilevante quantità di composti volatili del rum. L'esame dei concentrati così prodotti ha permesso di identificare numerosi composti organici tra i quali : 1-1, -tri metil-1,2-deidronaftalina, eptano-1-1 (—) oct-1-ene-3-ol ; metil salicilato e numerosi esteri di acidi grassi. Per lo studio à stato impiegato del rum grezzo, cioè prima dell'invecchiamento. Lo studio ha permesso di identificare dei composti che, si credeva si formassero durante l'invecchiamento.

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