

Analysis of the Flavor of Rum by Gas-Liquid Chromatography and Mass Spectrometry

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The volatile flavor components of a Jamaica rum have been analyzed by gas-liquid chromatography and mass spectrometry. Techniques applied to prepare samples for analysis were: condensation of head space vapor, extraction of rum with n-pentane and a mixture of n-pentane/ether (1:2), preparative fractionations on packed columns, and isolation of acids, phenols, lactones and bases from the n-pentane extract. Approximately 200 components were identified and classified into esters, acids, alcohols, phenols, lactones, carbonyl compounds, acetals, pyrazine derivatives, and hydrocarbons. Their concentrations in rum range from approximately 0.01 p.p.m. to 800 p.p.m. Based on the analytical results, an imitation of rum was prepared.

Introduction

Rum has a very strong flavor which depends upon various factors such as origin, age, and manufacturing process. Studies on the flavor of some varieties of this beverage have been undertaken by several investigators (1-11). Most of these works however, were only concerned with specific groups of compounds such as fusel oils or some low boiling components. A more extensive investigation was reported by Maarse and ten Noever de Brauw (12). They identified about 75 substances from Jamaica rum. A determination of the volatile, free fatty acids in four brands of rum was carried out by Nykänen et al. (13).

In spite of all these works however, the analysis of the flavor components of rum has not been satisfactorily completed. The analytical data available are not sufficient to prepare a good rum imitation and a preliminary gas chromatographic study of a rum flavor concentrate indicates the presence of considerably more components than those identified so far.

This investigation was concerned with the analysis of the flavor of a Jamaica rum containing 80% ethanol. Preparative and analytical gas chromatography, mass spectrometry, infrared spectroscopy, and in particular, combined gas chromatography and mass spectrometry (GC-MS) have been applied.

Experimental

Rum flavor condensate (A): A 2 l flask containing 1.5 l of rum was connected to a 20 ml flask, the former being kept at room temperature, the latter being cooled in a dry ice/acetone bath. After 36 hours, enough vapor was condensed to yield approximately 0.3 ml liquid which contained the very volatile constituents.

It was analyzed directly by GC-MS using an LKB 9000 instrument [column: 6 meter \times 4 mm I.D., copper, packed with 20% ethylene glycol-bis(cyanoethyl ether) on diatomaceous earth, 60-70 mesh].

Preparation of flavor extracts (B):

(a) 40 l of Jamaica rum were extracted for several days with predistilled n-pentane in a number of modified Kutscher-Stuedel extractors. The solvent was removed by careful distillation at atmospheric pressure through a Vigreux column until a residue of about 80 ml was left, corresponding to 0.2% of the original rum.

(b) After extraction with n-pentane and rum was submitted to a further extraction using n-pentane/ether (1:2). The extract obtained in this way contained large amounts of ethanol to be removed by washing the extract with water. After evaporation of the solvent, 20 ml of extract (0.05% of the rum) was obtained. The two samples were analyzed separately.

Isolation of acids (C): 5 ml n-pentane extract were extracted four times with 4 ml 6% aqueous NaHCO_3 solution in a separatory funnel. After acidification with 2N HCl, the organic acids were extracted from the aqueous solution with diethyl ether. The ether was evaporated until a residue of about 5 ml was left. Subsequently the free acids in this solution were esterified with diazomethane.

Isolation of phenols and lactones (D): The sample freed from the acids as described above was submitted to an extraction with a solution of 6% NaOH in water. By this procedure the phenols and lactones could be isolated as phenolates and sodium salts of hydroxy acids, respectively. Phenols and lactones themselves were obtained by acidification of the alkaline solution with 2N HCl followed by extraction with diethyl ether.

Isolation of organic bases (E): Organic bases were separated from the n-pentane extract by extracting 5 ml of this sample three times with 5 ml of 10% aqueous HCl in a separatory funnel followed by transformation of the hydrochlorides into free bases with 10% aqueous KOH and extraction with diethyl ether.

Preparative GC fractionations (F): Both the n-pentane extract and the n-pentane/ether extract were prefractionated on a 14 meter \times 15 mm I.D. steel column packed with 20% apiezon M on diatomaceous earth, 45-50 mesh [instrument: Bayer-Hupe(14)]. It was programmed non-linearly from 80°C to 230°C. Most of the 7 fractions collected in this way were submitted to further fractionations on smaller columns such as 8 meter \times 8 mm I.D. copper column packed with 20% ethylene glycol-bis(cyanoethyl ether) on diatomaceous earth (70-80 mesh) or 6 meter \times 8 mm I.D. copper

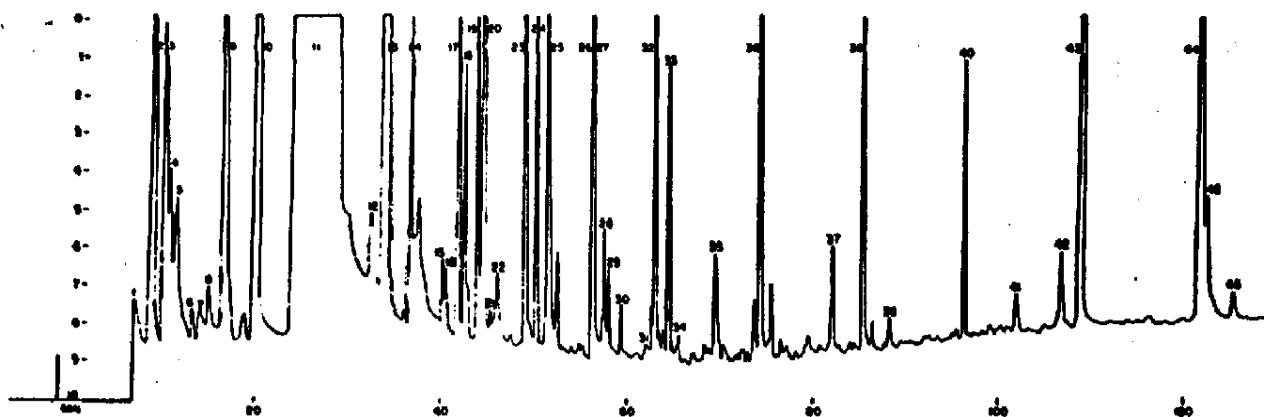


Figure 1. Capillary Gas Chromatogram of an n-Pentane Extract from Jamaica Rum.

Instrument: LKB Gas Chromatograph-Mass Spectrometer.

Conditions: 150 Meters \times 0.75 mm I.D. SF 96, 20 Minutes at Room Temperature, Then Programmed at 200°C to 2.5°C/min. Flow Rate 22 ml He/min, Sample Size 3 μ l.

column packed with 20% polyethylene glycol on diatomaceous earth (70-80 mesh), collecting 16 fractions every time.

Gas chromatography: For preparative GC two instruments were used: (a) a preparative gas chromatograph as described by Bayer et al.(14), equipped with an oven to allow the use of large diameter columns, a thermal conductivity cell, and a trapping device regulated by magnetic valves; (b) a Wilkens Aerograph Autoprep A-700 with a thermal conductivity cell and 16 traps. For analytical gas chromatography a Perkin-Elmer Fractometer F 6 and a Wilkens Aerograph 1520 were used, both equipped with flame ionization detector and thermal conductivity cell. The open tubular columns used were: 50 meters \times 0.25 mm I.D. stainless steel coated with silicone oil DC 550, 50 meters \times 0.25 mm I.D. stainless steel coated with polypropylene glycol, and 150 meters \times 0.75 mm I.D. stainless steel coated with silicone oil SF 96.

Infrared spectroscopy: Infrared spectra were recorded on a Perkin-Elmer Infracord Spectrophotometer Model 137. The samples were generally run in a 20% solution (solvent CCl_4) as films between sodium chloride plates.

Mass spectrometry: Mass spectra of isolated compounds were measured on a doubly focusing AEI MS 9 mass spectrometer at 70 eV*. Multi-component mixtures were analyzed on an LKB 9000 gas chromatograph/mass spectrometer at 70 eV, ion source temperature 270°C, separator temperature 250°C.

Results and Discussion

Vapor condensate (A): The vapor condensate represented a flavor enriched sample obtained in a very simple and smooth way which should be free of artifacts and contaminations. The gas chromatographic analysis of this sample was complicated by its high

*We thank K. P. Zeller and Dr. J. Heiss for running these samples.

ethanol content. However, using ethylene glycol-bis (cyanoethyl ether) as a highly polar phase with a long retention time for ethanol, valuable information was obtained on a number of low boiling constituents. They are included in Table I, listing all the components found in rum.

Identifications: Identification of approximately 200 substances was accomplished by analytical gas chromatography applying several phases and, in particular, by mass spectrometry. Reference mass spectra were taken from the literature and by measuring commercially available compounds. Many substances such as numerous asymmetrical acetals, 2-methyl-3-tetrahydrofuranone, 4-ethoxy-2-pentanone, and several esters were synthesized.

Isolated components were also analyzed by infrared spectrometry. An attempt was made to estimate roughly the concentrations of all the compounds in the original rum. This estimation was based on the amount of extract, the amount of isolated components, and peak areas in many gas chromatograms.

n-Pentane extract (B): Figure 1 shows a typical gas chromatogram of an extract obtained by extraction of Jamaica rum with n-pentane. The inlet valve to the mass spectrometer was closed during solvent elution from the column.

Apart from 3-methyl-1-butanol and 2-methyl-1-butanol (peak 11), the largest peaks in Figure 1 are ethyl esters of saturated carboxylic acids. Other components in high concentrations are 1,1-diethoxyethane, 1,1-diethoxy-2-methylpropane, 1,1-diethoxy-3-methylbutane, 1-ethoxy-1-(3-methylbutoxy)-ethane, furfural, 4-ethoxy-2-pentanone, 2-methyl-3-tetrahydrofuranone, 3-methylbutyl acetate, as well as two hydrocarbons with a molecular weight of 174 which were found to be 3,8,8-trimethyltetrahydronaphthalenes (TTN). Two more TTN-isomers, as well as a 3,8,8-trimethyldihydronaphthalene (TDN) with MW 172, were found in the last fraction obtained in the prefractionation of the n-pentane extract. The structure of these hydrocarbons was derived from their mass spectra, two of which are

Table 1. Constituents of Jamaica rum and their estimated concentration

Components	Found in Sample	Concentration in p.p.m.	Components	Found in Sample	Concentration in p.p.m.
Esters:					
ethyl formate	A	10	methyl n-hexadecanoate	F	0.3
isoamyl formate	F	2	ethyl n-hexadecanoate	B 43	50
ethyl acetate	A, B 2	200	n-propyl n-hexadecanoate	F	0.05
n-propyl acetate	A	0.5	isoamyl n-hexadecanoate	F	1
n-butyl acetate	F	0.01	ethyl palmitoleate	B 42	1.5
isobutyl acetate	F	1.5	ethyl n-heptadecanoate	F	0.05
isoamyl acetate	B 18	10	ethyl stearate	B 46	0.5
n-hexyl acetate	F	1	ethyl oleate	B 45	8
β-phenylethyl acetate	B 34	1	ethyl linolate	B 44	50
ethyl propionate	A, B 9	50	ethyl lactate	F	10
n-propyl propionate	F	0.2	monoethyl succinate	C 14	2
isobutyl propionate	F	0.5	diethyl succinate	B 31	0.8
isoamyl propionate	F	0.1	monoethyl citrate	C 18	1
ethyl n-butyrate	A, B 13	220	ethyl benzoate	B 31	0.5
n-propyl n-butyrate	F	0.03	methyl salicylate	D	0.15
isoamyl n-butyrate	F	1.5	ethyl (3-methoxy-4-hydroxybenzoate)	D	0.3
ethyl isobutyrate	F	8	ethyl (β-phenylpropionate)	F	0.5
ethyl n-valerate	B 20	40	ethyl (2-furancarboxylate)	F	0.1
isoamyl n-valerate	F	0.5			
ethyl isovalerate	B 16	2.5	Acids:		
ethyl (2-methylbutyrate)	B 15	2.5	acetic acid	F	35
ethyl n-hexanoate	B 25	40	propionic acid	C 1	1.5
isoamyl n-hexanoate	F	1	n-butyric acid	C 3	7.5
ethyl n-heptanoate	B 28	2.5	isobutyric acid	C 2	0.9
ethyl heptenoate	B 30	1.2	n-valeric acid	C 5	7.5
methyl n-octanoate	F	0.1	isovaleric acid	C 4	0.7
ethyl n-octanoate	B 32	15	2-methylbutyric acid	C 4	0.5
isoamyl n-octanoate	F	1	n-hexanoic acid	C 8	15
β-phenylethyl n-octanoate	F	0.1	isohexanoic acid	C 6	0.09
ethyl n-nonanoate	F	0.3	n-heptanoic acid	C 10	2.5
methyl n-decanoate	F	0.2	heptenoic acid	C 11	0.5
ethyl n-decanoate	B 36	25	n-octanoic acid	C 15	7.5
isobutyl n-decanoate	F	0.15	isooctanoic acid	C 12	0.03
isoamyl n-decanoate	B 39	1	n-nonanoic acid	C 16	0.05
β-phenylethyl n-decanoate	F	0.2	n-decanoic acid	C 17	0.5
ethyl n-undecanoate	F	0.13	β-ethoxypropionic acid	C 7	0.15
methyl n-dodecanoate	F	0.1	benzoic acid	C 13	0.4
ethyl n-dodecanoate	B 38	15	3-furancarboxylic acid	C 9	0.3
isoamyl n-dodecanoate	F	1	2-furancarboxylic acid	C 9	0.4
an ethyl dodecanoate	F	0.13			
an ethyl dodecanoate	F	0.15	Alcohols:		
ethyl n-tetradecanoate	B 40	5	methanol	A	0.05
isoamyl n-tetradecanoate	F	0.2	ethanol	A	—
ethyl n-pentadecanoate	B 41	0.8	n-propanol	A, B 1	7.5

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Table 1 (continued)

n-butanol	B 7	10	2-methyl-3-tetrahydrofuranone	F, B 12	5
isobutanol	B 3	100	Acetals:		
2-butanol	F	6	diethoxyethane	B 6	0.8
1-pentanol	F	2.5	1-methoxy-1-ethoxyethane	F	0.3
2-pentanol	F	0.5	1,1-diethoxyethane	A, B 10	320
3-pentanol	F	0.13	1-ethoxy-1-propoxyethane	F	1.2
2-methyl-2-butanol	F	0.2	1-ethoxy-1-butoxyethane	F	0.5
3-methyl-1-butanol	B 11	860	1-ethoxy-1-(2-methylpropoxy)-ethane	F	1.5
2-methyl-1-butanol	B 11	210	1-ethoxy-1-pentoxyethane	F	0.5
1-hexanol	F	2.5	1-ethoxy-1-(3-methylbutoxy)-ethane	B 24	10
2-hexanol	F	0.02	1-ethoxy-1-(2-methylbutoxy)-ethane	F	2.5
2-phenylethanol	F	0.5	1,1-dipropoxyethane	F	0.25
menthol	F	0.5	1-propoxy-1-(3-methylbutoxy)-ethane	F	2.5
Phenols:			1-butoxy-1-(3-methylbutoxy)-ethane	F	0.5
phenol	D	0.08	1,1-di-(2-methylpropoxy)-ethane	F	1.5
4-ethylphenol	D	0.25	1-(2-methylpropoxy)-1-(3-methylbutoxy)-ethane	F	5
2-methoxyphenol	D	0.25	1-pentoxy-1-(3-methylbutoxy)-ethane	F	0.08
4-methyl-2-methoxyphenol	D	0.05	1,1-di-(3-methylbutoxy)-ethane	F	7.5
4-ethyl-2-methoxyphenol	D	0.02	1-(3-methylbutoxy)-1-(2-methylbutoxy)-ethane	F	2.3
eugenol	D	0.08	1,1-diethoxypropane	F	1.2
isoeugenol	D	0.08	1-ethoxy-1-(2-methylpropoxy)-propane	F	0.25
Lactones:			1-ethoxy-1-(3-methylbutoxy)-propane	F	0.5
4-octalactone	D	0.01	1-propoxy-1-(3-methylbutoxy)-propane	F	0.12
γ-nonalactone	D	0.025	1,1-di-(2-methylpropoxy)-propane	F	1.3
γ-decalactone	D	0.025	1,1-diethoxybutane	F	0.12
6-decalactone	D	0.025	1,1-diethoxy-2-methylpropane	B 17	6
γ-dodecalactone	D	0.025	1-ethoxy-1-propoxy-2-methylpropane	F	1
6-dodecalactone	D	0.025	1-ethoxy-1-(2-methylpropoxy)-2-methylpropane	F	0.12
Carbonyl compounds:			1-ethoxy-1-(3-methylbutoxy)-2-methylpropane	F	5
acetaldehyde	A	0.5	1-propoxy-1-(2-methylpropoxy)-2-methylpropane	F	0.12
propionaldehyde	A	0.01	1-propoxy-1-(3-methylbutoxy)-2-methylpropane	F	0.12
isobutyraldehyde	A	0.25	1,1-di-(2-methylpropoxy)-2-methylpropane	F	0.5
isovaleraldehyde	B 4	1.8	1-(2-methylpropoxy)-1-(3-methylbutoxy)-2-methylpropane	F	0.8
2-methylbutyraldehyde	B 5	1.5	1,1-di-(3-methylbutoxy)-2-methylpropane	F	0.12
furfural	B 14	25	1-ethoxy-1-(2-methylpropoxy)-pentane	F	0.25
5-methylfurfural	F	1.2	1,1-di-(2-methylpropoxy)-pentane	F	0.05
benzaldehyde	F	2	1,1-diethyl-3-methylbutane	B 23	13
vanillin	D	0.25	1-ethoxy-1-(2-methylpropoxy)-3-methylbutane	F	5
acetone	A	0.25	1-ethoxy-1-(3-methylbutoxy)-3-methylbutane	F	4
2-butanone	F	0.03	1,1-dipropoxy-3-methylbutane	F	0.12
diacetyl	F	0.03	1-propoxy-1-(2-methylpropoxy)-3-methylbutane	F	0.08
2-pentanone	F	1.2	1-propoxy-1-(3-methylbutoxy)-3-methylbutane	F	0.25
3-penten-2-one	F	7	1,1-di-(2-methylpropoxy)-3-methylbutane	F	0.8
4-ethoxy-2-butanone	F	5	1-(2-methylpropoxy)-1-(3-methylbutoxy)-3-methylbutane	F	0.25
4-ethoxy-2-pentanone	B 19	7.5			
acetyl furan	F	1.2			
o-hydroxyacetophenone	D	0.01			

Table I (continued)

1,1-di-(3-methylbutoxy)-3-methylbutene	F	0.12	n-pentane (*)	A	0.05
1,1-diethoxy-2-methylbutane	F	2.5	2-methylpentane (*)	A	0.01
1,1-diethoxy-2-propanone	B 22	1.5	n-hexane (*)	A	0.05
			n-heptane (*)	A	0.05
Alkylpyrazines:			2-methylhexane (*)	A	0.025
2-methylpyrazine	E	0.5	2,3-dimethylpentane (*)	A	0.025
2,6-dimethylpyrazine	E	1.5	methylcyclohexane (*)	A	0.003
2,5-dimethylpyrazine	E	0.8	benzene (*)	F	0.12
2-methyl-6-ethylpyrazine	E	0.1	naphthalene (*)	F	0.1
2-methyl-3-ethylpyrazine	E	0.25	methylnaphthalene (*)	F	0.1
3,5-dimethyl-2-ethylpyrazine	E	0.1	anthracene (*)	F	0.13
2,5-dimethyl-3-ethylpyrazine	E	0.2			
Hydrocarbons:			Miscellaneous:		
3,8,8-trimethyl tetrahydronaphthalene	B 33	5	diethyl ether (*)	A	0.05
3,8,8-trimethyl tetrahydronaphthalene	B 35	1.2	2-methylfuran	A	0.05
3,8,8-trimethyldihydronaphthalene	F	0.25	dimethyl sulfide	A	0.12
			methylethyl sulfide	F	0.12
			o-chlorophenol (*)	D	0.05
			2,6-dichlorophenol (*)	D	0.025

A: vapor condensate

D: phenol/lecane sample

B: n-pentane extract, peak number refers to Figure 1

E: base sample

C: methylated acids, peak number refers to Figure 4

F: prefraction or fraction

(*) The origin of these compounds has not been completely clarified. However, the aliphatic hydrocarbons were found in sample A which was prepared without using

shown in Figures 2 and 3. All four TTN-isomers give the same mass spectra except for small differences in peak intensities. The mass spectral fragmentation of TDN is characterized by the loss of two methyl groups from position 8 (peaks at m/e 157 and m/e 142, metastable peak at 129) resulting in the methylnaphthalene system, the fragmentation of which yields most of the rest of the spectrum. In an analogous way, the spectra of the TTN-isomers can be interpreted.

The structures derived from the mass spectra were confirmed by synthesis. According to F. Tiemann (15, 16), ionene (I) was prepared in a condensation reaction from α -ionone using hydrogen iodide and amorphous phosphorus. Due to an easy dehydrogenation of ionene to dehydroionene (II) already reported by Tiemann, the synthetic product also contained about 10% of the dehydrogenated substance as evaluated by GC-MS analysis. Mass spectrum and retention

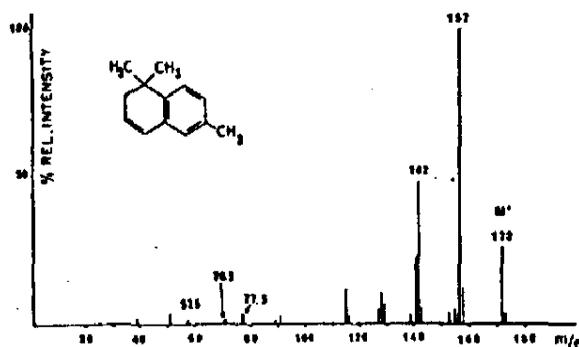


Figure 2. Mass Spectrum of 3,8,8-Trimethyldihydronaphthalene (TDN)

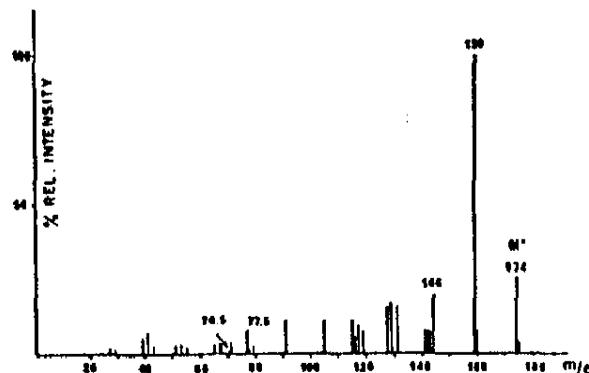
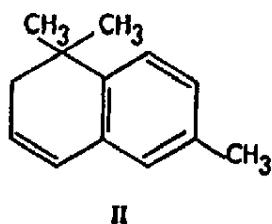
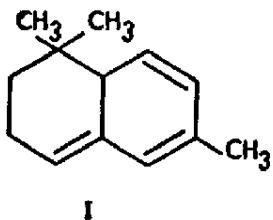


Figure 3. Mass Spectrum of 3,8,8-Trimethyltetrahydronaphthalene (TTN, B 33)

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time of the synthesized dehydroionene = 3,8,8-trimethyl-7,8-dihydronaphthalene are identical with those of TDN. As to ionene, only minor intensity changes are observed between its mass spectrum and the mass spectra of the four TTN compounds, but its retention time is a little shorter. The TTN compounds can be assumed to be isomers of ionene. The synthetic mixture of ionene and dehydroionene exhibits an extremely strong tar-like odor.

Mass spectral data for some other components found in the n-pentane extract are as follows (relative intensities in parentheses, base peak equals 100%):

4-ethoxy-2-pentanone, MW 130; 15 (7), 27 (7), 29 (10), 31 (6), 39 (7), 41 (9), 43 (100), 45 (58), 58 (4), 59 (5), 69 (9), 71 (10), 73 (16), 86 (14), 87 (6), 101 (18), 115 (6).

2-methyl-3-tetrahydrofuranone, MW 100; 15 (10), 27 (23), 28 (42), 29 (23), 31 (4), 42 (12), 43 (100), 44 (20), 45 (19), 55 (7), 56 (6), 72 (33), 73 (3), 85 (1), 100 (21).

isoamyl n-decanoate, MW 242; 27 (6), 29 (13), 41 (16), 43 (45), 55 (27), 57 (16), 69 (12), 70 (100), 71 (10),

81 (5), 85 (6), 95 (5), 101 (3), 115 (5), 129 (6), 143 (4), 155 (22), 172 (4), 173 (12), 187 (3), 199 (3), 227 (3), 242 (4).

The direct GC-MS analysis of the total n-pentane extract did not evaluate all of the constituents important to the rum flavor. This was noticed by an organoleptic test of the effluent from a packed column. Odors were perceived which were not consistent with the odor of the components identified so far. For that reason, a number of samples were prepared to enrich specific groups of constituents.

Acids (C): Figure 4 shows the chromatogram of methyl esters of acids isolated from the n-pentane extract. Identified were not only 14 saturated aliphatic carboxylic acids, heptenoic acid, β -ethoxypropionic acid, benzoic acid, 3-furancarboxylic acid, and 2-furancarboxylic acid, but also the monoethyl esters of succinic acid and citric acid.

Phenols and Lactones (D): Eleven phenolic compounds and six lactones were identified which may have considerable significance for the flavor. Two of the phenolic components, methyl salicylate and the ethyl ester of 3-methoxy-4-hydroxybenzoic acid are listed under esters in Table 1, o-hydroxyacetophenone and vanillin under carbonyl compounds.

Mass spectral data:
methyl salicylate, MW 152; 38 (5), 39 (22), 50 (4), 53 (6), 63 (14), 64 (15), 65 (23), 92 (60), 93 (14), 120 (100), 121 (31), 152 (48), 153 (4).

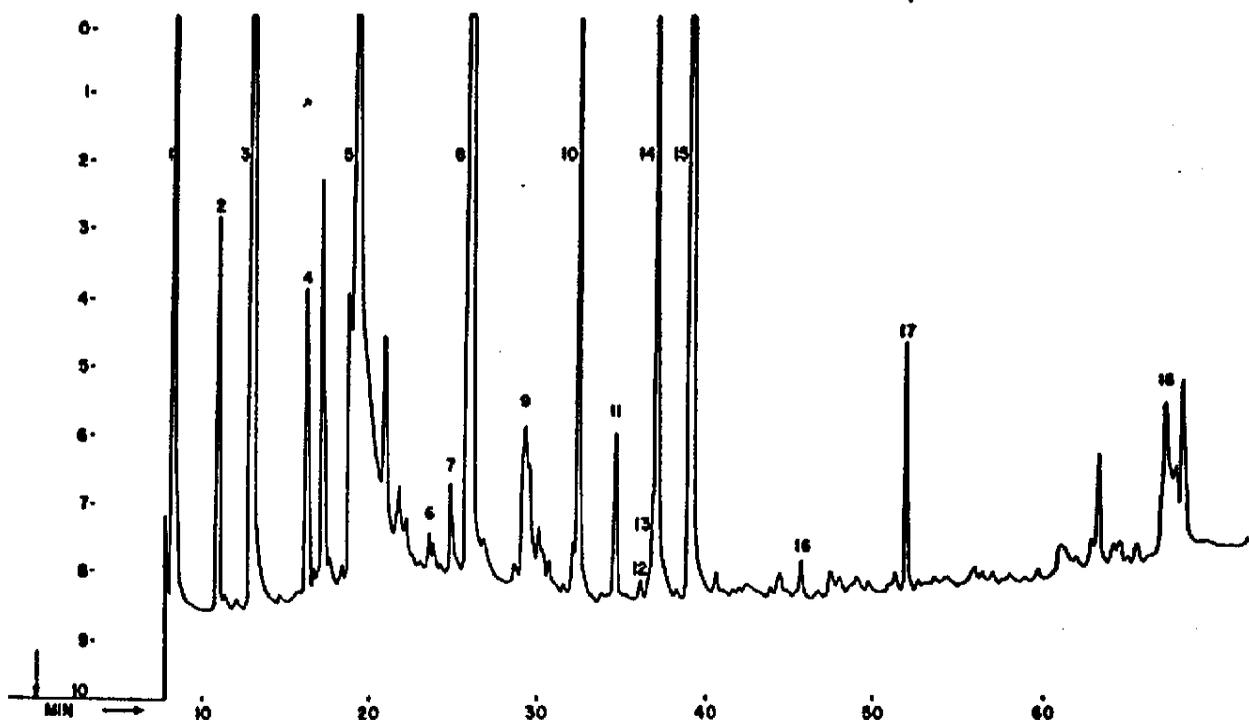


Figure 4. Capillary Gas Chromatogram of Methyl Esters in Ether.

Instrument: LKB Gas Chromatograph-Mass Spectrometer.

Conditions: 150 Meters \times 0.75 mm I.D. SF 96, Temperature Programmed from Room Temperature to 200°C at 2.5°C/min, Flow Rate 22 ml He/min, Sample Size 5 μ l.

ethyl (3-methoxy-4-hydroxybenzoate), MW 196; 39 (2), 41 (4), 53 (5), 65 (4), 67 (3), 77 (3), 79 (8), 109 (5), 110 (4), 123 (12), 151 (100), 152 (13), 153 (8), 168 (16), 181 (5), 196 (44), 197 (4).
4-ethylphenol, MW 122; 39 (6), 51 (4), 53 (4), 55 (2), 65 (4), 77 (16), 78 (3), 79 (3), 91 (6), 94 (2), 103 (2), 107 (100), 108 (10), 122 (35).
4-methyl-2-methoxyphenol, MW 138; 39 (18), 51 (12), 52 (8), 53 (10), 55 (19), 65 (8), 66 (12), 67 (14), 77 (19), 94 (5), 95 (35), 107 (13), 122 (10), 123 (88), 124 (9), 138 (100), 139 (12).

Interpretation of the γ - and δ -lactones, recognizable by their abundant mass spectral fragments m/e 85 and m/e 99, respectively, was based on their retention data and mass spectra reported by McFadden et al. (17).

Bases (E): This interesting sample exhibiting a slightly coffee-like odor, soluble in diethyl ether with a greenish yellow color and in ethanol with an orange color, contained at least 15 components, 7 of which were identified to be alkylpyrazines. They are the only nitrogen compounds found in rum. The major component among these alkylpyrazines is 2,6-dimethylpyrazine.

Mass spectral data for 2,6-dimethylpyrazine, MW 108; 37 (4), 38 (8), 39 (42), 40 (32), 41 (6), 42 (76), 52 (2), 53 (3), 54 (3), 64 (2), 66 (3), 67 (6), 81 (9), 93 (2), 107 (2), 108 (100), 109 (4).

Fractions (F): To enrich low concentrated neutral constituents prefractionations of the *n*-pentane extract and the *n*-pentane/ether extract followed by finer fractionations were carried out on packed columns. Numerous fractions were collected. Some of them consisted of only one component sufficiently pure to enable the measurement of infrared spectra. This was the case for several alcohols, esters, furfural, and 4-ethoxy-2-pentanone. Others were analyzed by GC-MS. Mass spectral data:

ethyl (β -phenylpropionate), MW 178; 27 (6), 29 (8), 39 (5), 51 (8), 65 (9), 77 (19), 78 (11), 79 (15), 91 (62), 104 (100), 105 (40), 107 (41), 133 (14), 149 (4), 178 (30).

β -phenylethyl *n*-decanoate, MW 276; 41 (4), 43 (7), 55 (6), 57 (8), 65 (3), 67 (3), 69 (6), 71 (8), 77 (3), 79 (3), 85 (5), 91 (4), 104 (100), 105 (31), 133 (1), 155 (4).

4-ethoxy-2-butanone, MW 116; 27 (14), 29 (16), 31 (33), 42 (9), 43 (100), 45 (20), 47 (2), 55 (14), 57 (5), 59 (21), 61 (4), 70 (5), 71 (14), 72 (30), 73 (7), 87 (20), 101 (11), 116 (1).

The last fraction collected in prefractionating the *n*-pentane/ether extract contained many acetals, both symmetrical and asymmetrical. It has not been clarified yet, whether all of them were originally present in rum or whether some were formed by transacetalization during extraction, concentration, and fractionation. The acetals improve the flavor of a synthetic rum by making it more homogeneous.

Flavor significance of identified substances and preparation of synthetic rum. Approximately 200 volatile components of rum were interpreted: esters,

acids, alcohols, phenols, lactones, carbonyl compounds, acetals, pyrazine derivatives, thioethers, and hydrocarbons. Their significance for the overall flavor is different. Some phenols, the 3,8,8-trimethylhydro-naphthalene isomers and some other highly odorous components may be of particular importance to the rum flavor. A good and full rum flavor however, is bound to the presence of almost all components in a concentration exceeding the threshold value. This became obvious in the approach to imitate the flavor of the analyzed rum. The best imitation was obtained by using all available substances found in rum.

A flavor mixture was prepared based on the proportions listed in Table I. An aliquot part of this sample was added to a mixture of 80% ethanol and 20% water, and the brown color of rum produced by adding a small amount of caramel. The mixture obtained in this way was found to be a quite good imitation of Jamaica rum.

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