THE JOURNAL OF AGRICULTURE
OF THE UNIVERSITY OF PUERTO RICO

Issued quarterly by the Agricultural Experiment Station of the University of Puerto Rico, Mayagüez Campus, for the publication of articles and research notes by staff members or others, dealing with scientific agriculture in Puerto Rico and elsewhere in the Caribbean Basin and Latin America.

Vol 71 APRIL 1987 No 2

Aging of high-test molasses rums[1]

Calixta S. de Torres, Zulma de Ayala and Marta I. Rivera[2]

ABSTRACT

Maturing of high-test molasses (HTM) rums was studied through the evaluation of changes in their composition during 1 and 3 years of aging. Spirits showed continuous and significant gains in total solids, acids, tannins, color, ethyl and methyl acetates, and isobutyl and isoamyl alcohols. Propyl alcohol remained unaffected. HTM rums 96° P reported more tannins and acids and less ethyl acetate and acetaldehyde than HTM rums 127° P. Data obtained from maturing HTM rums indicate that at different stages of the maturing period, tannin extraction and acid and ester formation in HTM rums proceed differently than they occur in blackstrap molasses (BM) rums.

INTRODUCTION

The Rum Industry of Puerto Rico, one of the main income producers of the island, brought about 14% of the gross insular income the past decade. The Rum Pilot Plant, established by the government to assist in the development of competitive technology for rum manufacture, has been conducting scientific research to attain this objective. During the last years intense work has been under way to evaluate the use of high-test molasses (HTM) for rum production. Results will help design modifications of traditional processes of the rum industry in the event high-test molasses instead of blackstrap molasses (BM) is to be used as raw material. The evaluation of the maturing of HTM rums could result in the recommendation of a longer or shorter period of aging of rums manufactured from the alternate raw material.

HTM is a heavy sugar cane syrup with 74 to 79% total sugars, 15 to 35% of which are inverted to avoid crystallization. Its high sugar concentration and its low ash content make this substrate a good raw material

[1]Manuscript submitted to Editorial Board November 25, 1985.

[2]Associate Chemists and Chemist, Ayerst-Wyeth Pharmaceutical, Inc., Guayama, P. R., and former Research Assistant, respectively, Rum Pilot Plant, Agricultural Experiment Station, Mayagüez Campus, University of Puerto Rico, Río Piedras, P. R. The authors appreciate Rum Pilot Plant Chemical Technician Luis A. Garcia's colaboration in the chromatographic analyses of samples.

for the elaboration of rum. Research on the evaluation and utilization of HTM has shown significant differences between the compositions of HTM and BM (9), in the rate of their alcoholic fermentations (6), the composition of fermented mashes obtained (5), and slops produced (8). A study on the development of maturity and HTM distillates was in order, particularly in the light of Arroyo's findings that rum made from sugar cane juice as raw material matured more slowly than BM spirits (1).

A review of the literature on the maturing of alcoholic beverages (10) reveals that during wood aging distillates undergo a series of definite organoleptic and chemical changes which characterize their quality. During aging, spirits decrease in total volume and pH and increase in degree proof, solids, esters, color, and furfural. The largest increase takes place during the first months of storage. Gains in aldehydes and a decrease of fusel oil result when calculations take into account changes in the original barreled volume. Proof of the spirit (2) affects the development of its maturity. Brau and Camacho (3) from 1953 to 1960, reported similar changes in composition of aged BM rums.

To ascertain the maturity of HTM rums, the Rum Pilot Plant has been analyzing the composition of aged samples of these spirits since 1980. This paper presents the results obtained during 2 and 3 years of aging of HTM rums and a preliminary comparison to the aging of BM rums, as reported by Brau and Camacho.

MATERIALS AND METHODS

Four different raw distillates produced at the Rum Pilot Plant from the fermentation of experimental HTM (147, 148, 150 and 151) were diluted with demineralized water to prepare batches of 96° and 127° P spirits. Six white oak-charred, used barrels, 208-liters total capacity, were cleaned with water and steam, each filled to 189 liters with a determined distillate, and properly identified. The barreled samples were stored in a concrete warehouse ventilated through two narrow louvered windows open to the outside. Average ambient conditions at the warehouse were 26° C temperature and 55% relative humidity.

During aging, after proper mixing of contents, one-liter samples were periodically (generally monthly) drawn from each barrel for analysis. Samples were analyzed for ethyl alcohol as degree proof, color, pH, total acidity, tannins, total solids, and congeners by the Official Analytical Methods of the Rum Pilot Plant (7). Gas chromatographic analysis of congeners quantitated acetaldehyde methyl and ethyl acetates, propyl, isobutyl, and isoamyl alcohols.[3] Although barreled spirits were 96° to

[3]Quantities mentioned from here on, not otherwise indicated, are mg/100 ml of the rum at 80° P.

127° P, contents of their congeners and tannins and total solids were expressed at 80° P; that is, the final dilution of the bottled rum product.

All distillates were aged for at least 16 months. After that minimum age, maturing of some rums was discontinued at determined periods of time and used for the manufacture of light HTM rums. For this purpose, contents of barrel 159 was removed from the warehouse at 16 months of age and contents of barrels 155 and 156, at 24 months of age; contents of barrels 157, 158, and 161 were allowed to age for 36 months.

To compare the development of maturity of HTM and BM rums manufactured at this station, we compared data from the present HTM study to pertinent data on aging BM rums, as reported by Brau and Camacho in 1960. Warehouse and ambient conditions affecting both studies were similar. Average compositions of the 105° P BM rum barreled by Brau and Camacho in white oak-charred used barrels were compared with those of 96° and 127° P HTM aging rums. Analytical methodology was similar in both studies, except for the determination of esters, fusel oil, and aldehydes. Since Brau and Camacho analyzed esters, fusel oil, and aldehydes, respectively, as total esters, total aldehydes and total fusel oil, similar HTM rum data were rearranged to make them comparable. The analyses of methyl and ethyl acetates of each HTM rum sample were added and tabulated as total esters; propyl, isobutyl, and isoamyl alcohol contents were added and reported as total fusel oil. On the basis of rum analysis experience, analyses of acetaldehyde in HTM rums were assumed to correlate with the analyses of total aldehydes reported by Brau and Camacho. Although the average raw BM rum was significantly heavier than HTM spirits, a preliminary or tentative comparison of the trend of changes of tannins, total acids, aldehydes, esters, and fusel oil of aging HTM and BM rums was considered of interest.

Data on the compositions of aging rums, including the data reported by Brau and Camacho, were submitted to a statistical evaluation. Equations for all maturity curves were determined and plotted.

RESULTS AND DISCUSSION

Tables 1 and 2 present, respectively, the composition of HTM-147 distillate contained in barrel No. 155 and HTM-148 distillate contained in barrel No. 156, both stored at approximately 96° P. Tables 3, 4 and 5 present, respectively, the composition of HTM-148, 150, and 151 distillates, stored in barrels No. 157, 158, and 161, all three barreled at approximately 127° P.

Table 6 presents a comparison of the changes of concentration of acids, aldehydes, esters and tannins of HTM 96° and 127° P and the BM 105° P rum reported by Brau and Camacho during 24- and 36-month maturing periods.

TABLE 1.—*Composition of HTM-147 rum aged in barrel No. 155 for 24 months*

Composition	Age (months)																	
	1	2	3	4	5	6	7	10	11	12	13	14	15	16	17	21	22	24
Alcohol (°P)	96.1	97.0	97.0	96.9	95.4	96.7	97.4	97.4	98.0	98.8	98.1	98.3	98.1	98.2	99.0	99.4	98.6	97.4
Color (A)	0.097	0.101	0.131	0.146	0.143	0.193	0.209	0.248	0.272	0.301	0.305	0.314	0.342	0.347	0.370	0.438	0.463	0.480
pH	5.5	5.0	4.9	5.0	4.6	4.8	4.4	4.5	4.3	4.7	4.3	4.4	4.5	4.6	4.5	4.7	4.3	4.3
	mg/100 ml at 80°P																	
Total acidity	1.1	2.1	3.2	4.3	4.0	7.2	8.0	10.6	12.1	13.1	13.4	14.9	16.6	17.7	19.1	21.0	23.3	25.4
Acetaldehyde	0.2	0.4	0.4	0.4	0.3	0.5	0.6	0.4	0.4	0.6	0.6	0.6	0.5	1.6	1.8	2.1	1.7	2.6
Methyl acetate	0.1	0.2	0.2	0.2	0.2	0.3	0.4	0.6	0.7	0.8	0.6	0.8	1.0	1.3	1.8	1.2	1.3	1.4
Ethyl acetate	2.4	3.5	3.6	4.0	2.4	3.7	4.3	5.3	5.6	5.9	6.0	6.6	6.5	7.3	7.7	9.8	10.0	8.7
Propyl alcohol	3.7	4.2	4.2	3.7	4.2	4.0	6.3	6.2	6.0	6.1	6.4	6.4	5.8	5.8	5.7	5.8	6.3	6.2
Isobutyl alcohol	6.5	8.3	8.5	8.3	8.5	8.5	8.4	8.2	8.2	8.5	8.4	8.4	8.0	5.8	5.3	7.5	5.3	5.6
Isoamyl alcohol	1.5	2.0	1.9	1.9	2.1	2.3	2.4	2.6	2.6	2.7	2.8	2.9	2.8	2.6	2.6	3.5	3.4	3.5
Tannins	1.8	2.2	3.8	5.2	6.1	7.0	8.1	12.0	12.0	12.8	12.9	13.5	15.7	15.1	15.4	15.4	17.8	21.7
Total solids	12.0	12.9	13.8	17.2	22.6	25.2	26.3	36.1	37.2	43.4	42.4	45.9	49.6	50.2	51.7	53.8	57.1	62.8

TABLE 2.—*Composition of HTM-148 rum, unaged and aged in barrel No. 156 for 24 months*

Composition	Age (months)																	
	0	2	3	4	5	6	7	10	11	12	13	14	15	16	17	21	22	24
Alcohol (°P)	95.9	91.6	94.6	93.8	94.0	94.1	94.4	94.8	94.9	94.7	94.8	94.4	94.2	95.5	95.8	96.2	96.3	96.3
Color (A)	0	0.108	0.131	0.135	0.155	0.206	0.215	0.259	0.268	0.276	0.333	0.276	0.369	0.354	0.362	0.400	0.391	0.446
pH	7.4	5.0	4.9	4.8	4.8	4.9	4.7	4.7	4.7	4.7	4.6	4.6	4.4	4.4	4.6	4.5	4.6	4.4
	mg/100 ml at 80°P																	
Total acidity	0	4.1	6.0	6.7	5.6	6.2	7.7	9.5	10.9	11.5	12.3	13.2	14.7	16.1	17.3	18.9	21.7	23.1
Acetaldehyde	0	0.4	0.2	0.7	0.4	0.3	0.5	0.6	0.6	1.4	1.7	0.7	0.7	2.1	1.2	2.2	1.0	2.4
Methyl acetate	0	0.2	0.2	0.1	0.2	0.2	0.4	0.4	0.4	0.4	0.6	0.6	0.7	0.6	0.1	0.8	0.8	1.2
Ethyl acetate	1.3	0.9	1.8	1.8	1.8	1.8	2.6	2.8	3.3	3.2	3.9	4.3	4.7	5.0	2.6	6.6	4.2	8.6
Propyl alcohol	5.6	6.0	5.9	6.5	5.5	5.3	6.0	5.8	6.3	5.2	5.9	6.2	6.5	7.3	4.8	5.5	5.5	6.0
Isobutyl alcohol	2.3	2.5	2.6	6.0	2.4	2.3	2.9	2.8	3.3	2.8	2.9	2.9	3.4	1.8	2.0	2.5	1.7	2.0
Isoamyl alcohol	1.3	1.6	1.9	1.9	1.9	2.2	2.4	2.6	2.9	2.4	2.4	2.8	2.8	2.5	2.6	3.3	274	3.4
Tannins	0	4.1	6.0	6.7	5.6	6.0	6.6	8.1	9.0	9.4	14.1	14.4	16.6	14.9	14.5	14.6	22.1	22.1
Total solids	0	16.0	19.6	22.5	24.8	25.8	27.5	34.8	38.8	38.5	40.2	43.4	46.5	46.7	48.8	50.2	50.3	57.7

TABLE 3.—*Composition of HTM-148 rum, unaged and aged in barrel No. 157 for 36 months*

Composition	Age (months)																				
	0	1	5	6	7	8	9	10	11	12	13	14	15	16	17	18	21	25	29	33	36
Alcohol (°P)	126.0	120.7	121.2	121.2	121.4	121.4	120.1	120.1	121.3	121.2	121.5	121.5	121.2	120.3	121.7	121.8	121.6	122.8	118.0	120.2	121.0
Color (A)	0	0.137	0.208	0.167	0.197	0.222	0.228	0.269	0.279	0.310	0.328	0.284	0.309	0.323	0.349	0.365	0.439	0.453	0.463	0.513	0.767
pH	5.4	5.5	5.2	5.1	5.0	5.2	5.3	5.0	4.9	4.9	5.0	4.7	5.1	5.2	4.8	4.8	4.9	4.4	4.4	4.3	3.6
	mg/100 ml at 80°P																				
Total acidity	0.3	1.0	2.9	3.8	4.6	4.8	5.6	6.1	6.9	7.0	9.0	9.8	9.4	9.9	10.5	10.5	12.8	14.5	18.1	20.0	24.2
Acetaldehyde	0.7	0.3	0.4	0.5	0.4	0.5	0.6	0.5	2.0	2.4	2.0	2.1	2.2	2.6	3.1	2.8	2.9	3.5	3.9	5.0	5.1
Methyl acetate	0.3	0.1	0.2	0.2	0.3	0.3	0.3	0.4	0.7	1.0	0.5	0.9	1.1	1.0	1.5	1.2	1.4	1.2	1.1	1.4	1.6
Ehtyl acetate	2.0	2.1	2.6	2.7	3.0	3.3	3.1	3.6	4.2	4.3	4.3	5.2	5.1	6.7	7.2	6.9	7.3	8.2	8.4	10.7	13.5
Propyl alcohol	7.5	6.5	6.8	6.3	6.3	7.3	5.8	6.2	7.7	6.6	8.4	8.2	6.7	7.1	7.0	6.8	7.2	6.4	7.8	8.0	8.3
Isobutyl alcohol	4.9	8.7	9.0	8.4	8.4	9.1	8.3	7.6	5.3	4.9	6.6	5.3	5.1	5.2	5.1	5.1	5.3	5.2	7.9	8.2	8.5
Isoamyl alcohol	1.0	1.3	1.6	1.8	1.8	1.9	1.8	1.8	1.9	1.9	1.9	2.5	2.1	2.1	2.4	2.4	2.3	2.3	2.4	2.6	2.8
Tannins	0	2.3	5.8	5.7	6.7	13.5	7.5	9.6	7.1	7.7	8.5	8.7	10.1	10.3	11.0	11.0	14.0	14.6	13.9	14.8	20.4
Total solids	0	10.6	17.4	18.5	20.0	21.4	22.3	25.2	30.4	29.3	30.0	32.4	35.6	38.3	39.2	35.7	38.7	46.9	48.5	51.1	61.4

TABLE 4.—*Composition of HTM-150 rum, unaged and aged in barrel No. 158 for 36 months*

	Age (months)																				
Composition	0	1	5	6	7	8	9	10	11	12	13	14	15	16	17	18	21	25	29	33	36
Alcohol (°P)	126.0	120.3	120.7	120.7	121.4	121.6	122.2	120.7	121.3	120.9	121.5	121.4	121.6	121.2	121.4	121.7	121.5	122.9	117.8	119.5	121.3
Color (A)	0	0.081	0.126	0.155	0.152	0.208	0.215	0.222	0.246	0.250	0.328	0.254	0.272	0.296	0.452	0.361	0.419	0.419	0.415	0.472	0.519
pH	5.4	5.8	5.8	5.7	5.7	5.1	5.1	5.0	5.2	5.2	5.0	5.0	5.2	5.0	4.4	4.9	5.0	4.6	4.6	4.7	3.6
	mg/100 ml at 80°P																				
Total acidity	0.3	0.9	1.7	2.3	2.7	3.1	3.8	4.3	4.8	5.6	6.4	6.3	6.6	7.7	8.3	8.7	9.6	10.4	14.8	16.3	18.7
Acetaldehyde	0.7	0.5	0.4	0.4	0.4	0.4	1.7	2.4	1.9	1.8	2.0	2.1	2.4	2.5	5.4	3.0	3.3	4.0	3.8	5.4	5.4
Methyl acetate	0.3	0.1	0.2	0.2	0.3	0.3	0.8	1.4	0.7	0.7	0.5	1.0	1.3	1.6	3.4	1.7	1.8	2.2	1.5	2.9	2.4
Ehtyl acetate	2.0	2.3	2.4	2.5	2.5	2.7	4.1	5.3	3.8	4.1	4.3	5.3	5.5	6.2	12.0	6.4	6.7	7.1	7.5	9.6	11.1
Propyl alcohol	7.5	6.2	5.8	5.2	5.5	5.5	6.3	6.1	6.9	6.8	8.4	6.8	6.9	7.0	3.9	6.4	6.7	6.8	7.9	7.7	8.0
Isobutyl alcohol	4.9	8.1	8.2	8.0	8.0	8.1	4.9	5.0	5.0	5.2	6.5	5.2	5.2	5.1	1.3	4.9	5.2	5.4	7.9	7.7	8.2
Isoamyl alcohol	1.0	1.0	1.2	1.2	1.3	1.4	1.4	1.4	1.5	1.6	1.8	1.6	1.6	1.6	2.5	1.6	1.8	1.8	2.0	2.0	2.1
Tannins	0	1.4	3.1	3.7	4.1	4.5	6.4	6.8	6.8	5.0	8.5	6.8	7.6	7.6	13.8	9.1	10.8	13.7	12.1	12.4	15.2
Total solids	0	8.0	11.9	13.8	17.9	17.1	18.8	19.4	22.7	23.6	24.7	28.2	28.4	30.1	33.5	29.2	33.5	38.3	39.1	42.3	44.6

TABLE 5.—*Composition of HTM-151 rum, unaged and aged in barrel No. 161 for 36 months*

	Age (months)																				
Composition	0	1	5	6	7	8	9	10	11	12	13	14	15	16	17	18	21	25	29	33	36
Alcohol (°P)	128.0	122.1	123.3	123.0	123.5	121.7	121.7	121.4	123.8	123.0	122.7	122.8	123.6	123.1	122.7	123.3	123.6	124.4	124.5	125.9	125.9
Color (A)	0	0.076	0.158	0.187	0.178	0.187	0.199	0.214	0.222	0.251	0.326	0.260	0.272	0.287	0.304	0.329	0.380	0.420	0.437	0.483	0.551
pH	6.1	5.6	5.5	5.4	5.3	5.3	5.2	5.3	4.9	5.0	4.7	4.8	5.0	5.0	4.8	4.8	4.9	3.5	4.5	4.4	3.4
	mg/100 ml at 80°P																				
Total acidity	0	1.3	2.6	2.6	3.6	4.1	4.5	5.3	6.4	6.7	7.1	8.0	8.2	9.1	9.1	9.5	12.8	14.4	17.3	19.1	21.5
Acetaldehyde	2.1	—	3.5	4.1	2.6	3.3	4.1	5.7	6.1	4.2	5.7	4.9	2.2	4.6	4.6	5.0	6.3	6.7	7.0	5.8	5.3
Methyl acetate	T[y]	—	1.0	0.7	0.5	0.6	0.5	3.5	3.9	1.2	4.0	1.8	0.6	1.2	0.9	1.8	1.5	4.0	4.4	2.4	1.8
Ehtyl acetate	2.3	—	3.6	4.2	4.8	4.8	3.1	10.1	10.8	6.6	11.8	4.2	3.9	7.4	4.9	9.5	11.1	13.4	15.7	14.8	13.2
Propyl alcohol	3.0	—	2.7	2.8	3.2	4.7	3.0	4.2	3.0	4.2	2.9	3.0	4.2	2.9	3.7	2.8	3.9	3.1	3.0	3.1	4.1
Isobutyl alcohol	0.9	—	0.9	0.7	0.7	0.7	1.0	1.1	0.8	1.0	1.0	0.8	0.8	0.7	1.0	0.9	1.5	1.1	0.8	1.0	1.6
Isoamyl alcohol	0.3	—	1.1	1.3	1.6	1.5	0.8	1.7	1.8	1.8	0.8	2.0	1.9	1.8	2.1	2.0	2.3	2.7	2.3	2.3	2.4
Tannins	0	2.5	10.5	11.0	5.8	7.6	13.9	8.1	9.5	9.9	7.8	10.9	11.3	12.4	12.4	13.0	12.4	13.1	12.6	13.3	16.5
Total solids	0	11.3	16.9	16.9	18.9	20.0	21.8	33.7	25.8	26.5	29.4	30.7	32.9	33.0	36.2	34.3	37.3	47.6	47.7	49.3	50.8

TABLE 6.—*Average composition[1] of 96° and 127°P HTM rums and 105°P BM rum[2] unaged and aged for 36 months*

	Total acids			Total aldehydes			Total esters			Total tannins			Total fusel oil		
Age months	HTM-96°P	BM-105°P	HTM-127°P	HTM-96°P	BM-105°P	HTM-127°P	HTM-96°P	BM-105°P	HTM-127°P	HTM-96°P	BM-105°P	HTM-127°P	HTM-96°P	BM-105°P	HTM-127°P
0	0	1.9	0.2	0	10.2	1.2	1.3	11.2	2.3	0	1.7	0	9.2	88.3	10.4
0.46	—	3.7	—	—	10.2	—	—	15.8	—	—	2.2	—	—	83.3	—

0.92	—	4.6	—	—	10.2	—	—	15.8	—	—	2.8	—	—	88.4	—
1.0	1.1	—	1.1	0.2	—	0.4	2.5	—	2.3	1.8	—	2.1	11.7	—	16.2
1.4	—	6.5	—	—	11.2	—	—	19.5	—	—	3.0	—	—	83.7	—
1.8	—	6.5	—	—	11.2	—	—	23.3	—	—	3.3	—	—	93.0	—
2.0	3.1	—	—	0.4	—	—	2.4	—	—	3.2	—	—	12.3	—	—
3.0	4.6	6.5	—	0.3	11.2	—	2.9	22.3	—	4.9	4.4	—	12.5	—	—
4.0	5.5	8.4	—	0.6	11.2	—	3.1	25.1	—	6.0	5.7	—	14.1	97.7	—
5.0	4.8	—	2.4	0.4	—	1.4	2.3	—	3.4	5.8	—	6.5	16.9	—	12.4
6.0	6.7	10.2	2.9	0.4	10.2	1.7	3.0	24.2	3.5	6.5	7.0	6.8	11..9	88.4	11.9
7.0	7.8	—	3.6	0.6	—	1.1	4.1	—	3.8	7.4	—	5.5	13.8	—	12.3
8.0	—	—	4.0	—	—	1.4	—	—	4.0	—	—	8.5	—	—	13.4
9.0	—	12.1	4.6	—	10.2	2.1	—	33.5	3.9	—	8.8	9.3	—	93.0	11.0
10.0	10.0	—	5.2	0.5	—	2.7	4.5	—	8.1	10.0	—	8.2	13.7	—	11.7
11.0	11.5	—	6.0	0.5	—	3.3	5.0	—	8.1	10.5	—	7.8	14.4	—	11.7
12.0	12.3	14.9	6.4	1.0	9.3	2.8	5.2	29.8	6.0	11.1	9.9	7.5	13.8	102.0	11.0
13.0	12.8	—	7.5	1.2	—	3.2	5.6	—	9.7	13.5	—	8.3	14.6	—	13.2
14.0	14.0	—	8.0	0.6	—	3.0	6.1	—	6.1	14.0	—	8.8	14.5	—	11.8
15.0	15.6	—	8.1	0.6	—	2.3	6.4	—	5.8	16.2	—	9.7	14.5	—	11.5
16.0	16.9	17.7	8.9	1.8	12.1	3.2	7.2	35.3	8.1	15.0	10.5	10.1	13.2	—	11.2
17.0	18.2	—	9.3	1.5	—	4.4	6.2	—	9.9	15.0	—	12.4	11.6	—	9.7
18.0	—	—	9.6	—	—	3.6	—	—	9.2	—	—	11.0	—	—	10.8
20.0	—	20.5	—	—	13.0	—	—	42.8	—	—	11.4	—	—	—	—
21.0	22.3	—	11.7	2.2	—	4.2	9.2	—	10.0	15.0	—	12.4	14.0	—	12.0
22.0	22.5	—	—	1.4	—	—	8.1	—	—	20.0	—	—	12.4	—	—
24.0	24.2	22.3	—	2.5	13.9	—	9.9	45.6	—	21.9	13.5	—	13.3	102.0	—
25.0	—	—	13.1	—	—	4.7	—	—	12.1	—	—	13.8	—	—	11.6
29.0	—	—	16.7	—	—	4.9	—	—	12.8	—	—	12.9	—	—	13.9
30.0	—	28.8	—	—	14.9	—	—	51.2	—	—	14.1	—	—	121.0	—
33.0	—	—	18.5	—	—	5.4	—	—	13.9	—	—	13.5	—	—	14.2
36.0	—	31.6	21.5	—	15.8	5.3	—	44.6	14.5	—	16.6	17.4	—	126.0	15.2

[1]Mg/100 ml at 80°P.

[2]From Brau and Camacho.

Figures 1 to 4, 6, 8 and 10, present to maturity curves of the average concentration vs. age of several components of the two 96° and the three 127° P HTM rums. Figures 5, 7, 9, 11 and 12 present comparative maturity curves of HTM and BM rums, obtained from data in table 6.

Changes in composition of the HTM 127° P rum samples drawn from barrel No. 159 during 16 months were found to fit satisfactorily into the average pattern of changes in composition of 127° P HTM spirits aged for 36 months (barrels No. 157, 158, and 161). These average changes and those of 96° P HTM rums, evaluated during 24 and 36 months of aging, were as follows:

Ethyl alcohol (figure 1)

Aging spirits decreased in alcohol content immediately after the barreling date (T=0). This drop in proof is caused mainly by the residual moisture contained in the wood of the barrel. Following this initial dilution, ethyl alcohol started to concentrate as controlled by the equilibrium established between the relative humidity of the warehouse and the wood of the barrel. Although both 96° and 127° P HTM rums followed this general trend, significant differences were observed. HTM 127° P rum presented a relatively large drop in ethyl alcohol after the barreling date and fluctuations of proof in an irregular pattern during aging. It did not attain the original alcohol content for the duration of the 3-year maturing period. HTM rum 96° P attained the original proof around 7 months after the barreling data and continued to concentrate ethyl alcohol up to 21

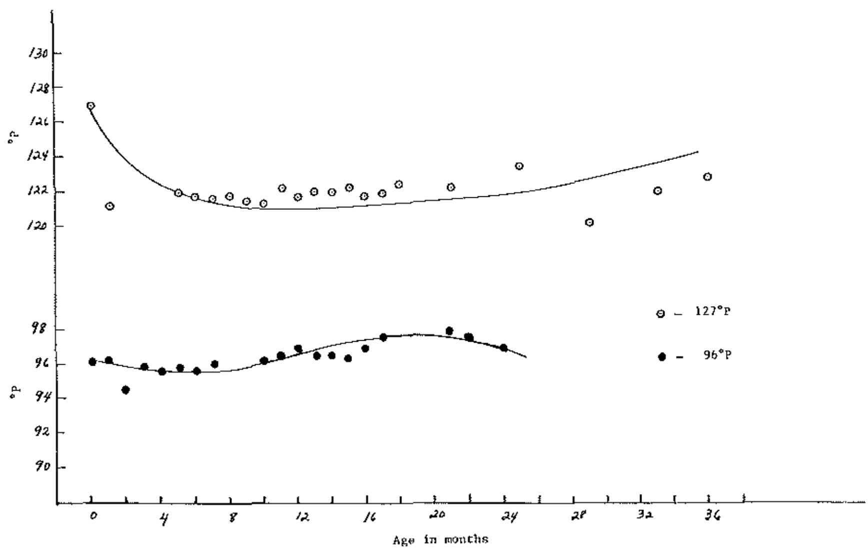

FIG. 1.—Changes in ethyl alcohol content (°P) of high-test molasses rums barreled at 96°P and 127°P during aging.

months of age. Then a decrease in proof was determined, indicating higher ethyl alcohol than water evaporation during the last period of aging. Changes in composition vs. age of other volatile components also ought to have been affected by evaporation.

Total solids (figure 2)

Solids in aged rums are derived by extraction from the wood of the barrel. As all barrels are manufactured from standard grade white oak, the extracts are similar in character and impart to the final product a definite particular quality. HTM rum 127° P extracted 26 mg total solids during the first year, approximately 18 during the second, and 9 during the third, for a total of 53 mg during the 36-month maturing period. HTM rum 96° P extracted a total of 60 mg solids at the end of the 24-month maturing period: 37 during the first year and 23 during the second. HTM rum 96° P reported 1.4 times more solids than HTM 127° P rum at the end of the first 2 years of aging. The alcoholic strength of the spirit appears to have affected total solids extraction in an inverse relation: the higher the proof the lower the extraction of solids. True extraction at the proof of the sample (barrel proof) is less significant, when one consid-

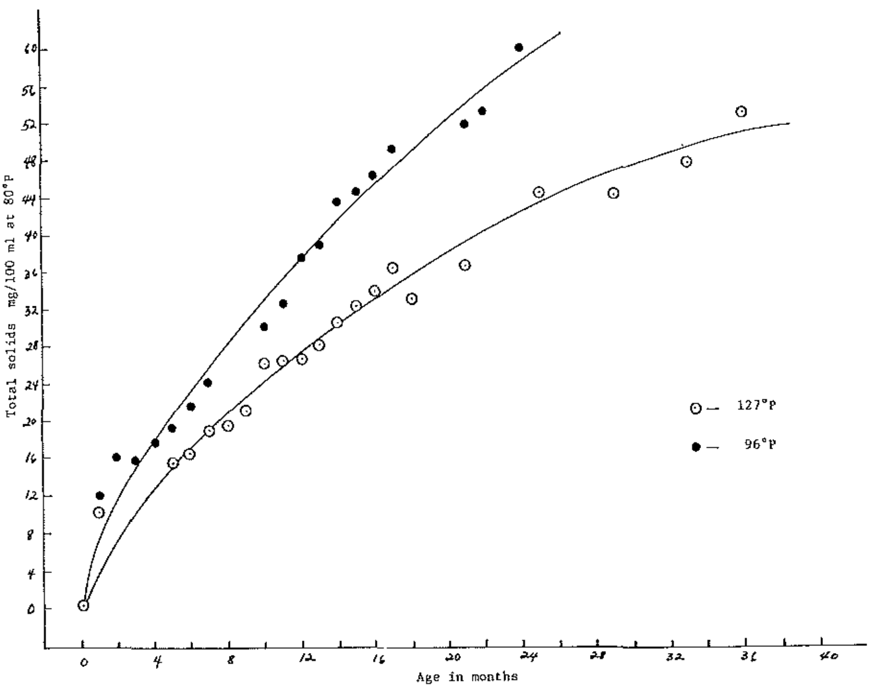

FIG. 2.—Changes in total solids content of high-test molasses rums barreled at 96° and 127°P during aging.

ers that the mathematical dilution of the aging rums to 80° P lowers the true composition of 127° P samples 1.3 times more than that of 96° P spirits.

Color (figure 3)

Color is strictly due to substances extracted from the barrel. The color of rum changes from colorless to light and deep yellow, then to amber and finally to reddish brown. Since color development is due to progressive extraction from wood, changes in color of aging distillates follow a pattern similar to that of solids extraction. It was observed that, at the same aging period, colors of HTM rums 96° P were consistently darker than those of HTM rums 127° P.

Tannins (figures 4 and 5)

Wood extraction is solely responsible for the tannins (tannic acid) in rums and they are part of the total solid content of aged spirits. In general, gains of total solids and tannins in HTM during aging follow the curve of a hyberbola, leading to an asymptotic approach to a maximum value, that appears to indicate that extraction is limited (4).

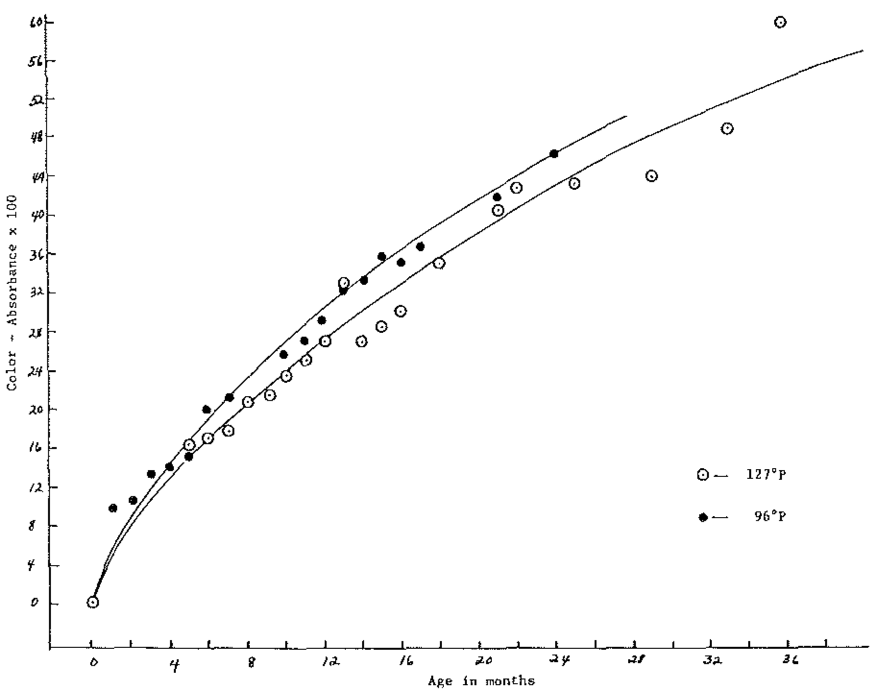

FIG. 3.—Changes in the color of high-test molasses rums barreled at 96° and 127°P during aging.

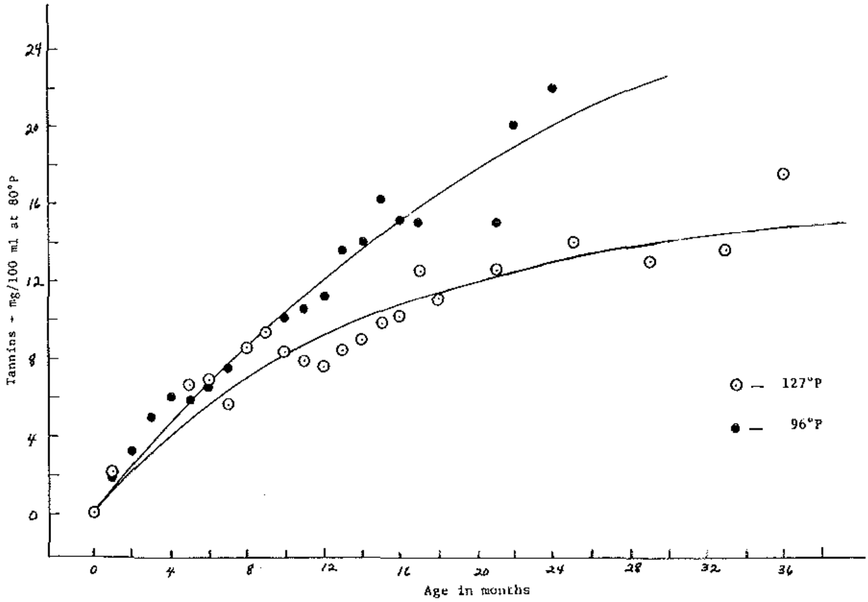

FIG. 4.—Changes in tannin content of high-test molasses rums barreled at 96° and 127°P during aging.

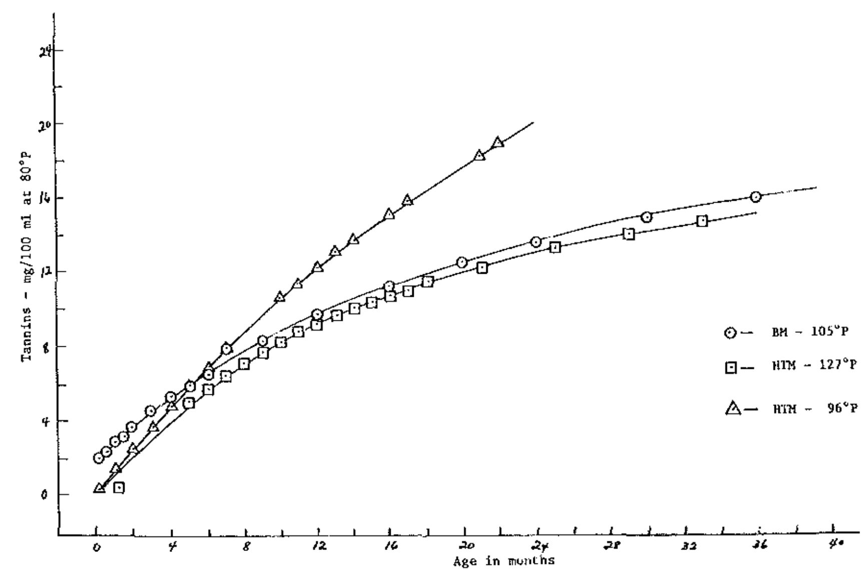

FIG. 5.—Changes in tannin content of high-test and blackstrap molasses rums during aging.

Tannins in aged HTM rums were found to constitute approximately 32% total solids in both 96° and 127° P spirits. During the first 6 months of aging, both 96° and 127° P spirits extracted approximately the same amount of tannins: 6.5 to 7.0 mg/100 ml, although there was 31° P difference between the samples. At the end of the first year HTM rum 127° P had extracted 8 mg tannins, approximately 6 during the second and 3 during the third, for a total of 17 during the 36-month maturing period. HTM rum 96° P had extracted 11 mg during the first year and 11 during the second for a total of 22 during the 24-month maturing period. HTM rum 96° P reported an average of 1.6 times more tannins than HTM rum 127° P in the period from 1 to 2 years of aging, in an inverse relation to the proof of the spirit.

When HTM aging rum data were compared to the results of Brau and Camacho (3), it was found that during the first 6 months of aging the BM rum had extracted approximately the same amount of tannins extracted by the HTM rums. It appears that during the first month of aging tannins are extracted independently of origin or proof of the sample. During the period comprising the last 18 months of the 24 months of aging, the three rums extracted tannins in an inverse relation to the proof of the sample, but with interesting differences in the slopes of the curves. It appears that during that period 105° P BM rum significantly slowed its rate of

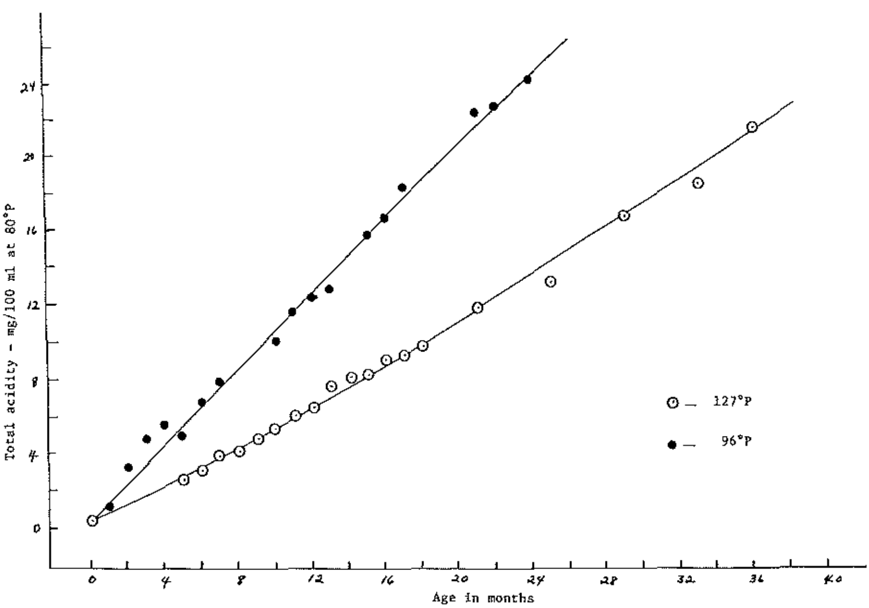

FIG. 6.—Change in total acidity of high-test molasses rums barreled at 96° and 127°P during aging.

tannin extraction to the point of reaching 3 years of age with fewer tannins than the 127° P HTM rum.

Total acidity (figures 6 and 7)

Total acids comprise fixed acids and volatile acids; tannic acid is one of the fixed acids in aged rums. Although the mechanism for acid formation during wood aging is not well known, it is believed that fixed acids are extracted from the barrel and volatile acids are formed by oxidation reactions.

Determinations of pH during the maturing period showed a continuous decreasing tendency. Independently of the initial pH, all aging HTM rums attained 4.7 to 5.0 pH at the end of the first year, 4.2 to 4.4 at the end of the second year, and 127° P rums reached 3.5 pH at the end of the third year.

Gains of total acids in HTM rums followed a straight line development during aging. HTM rums 127° P showed a continuous increase in total

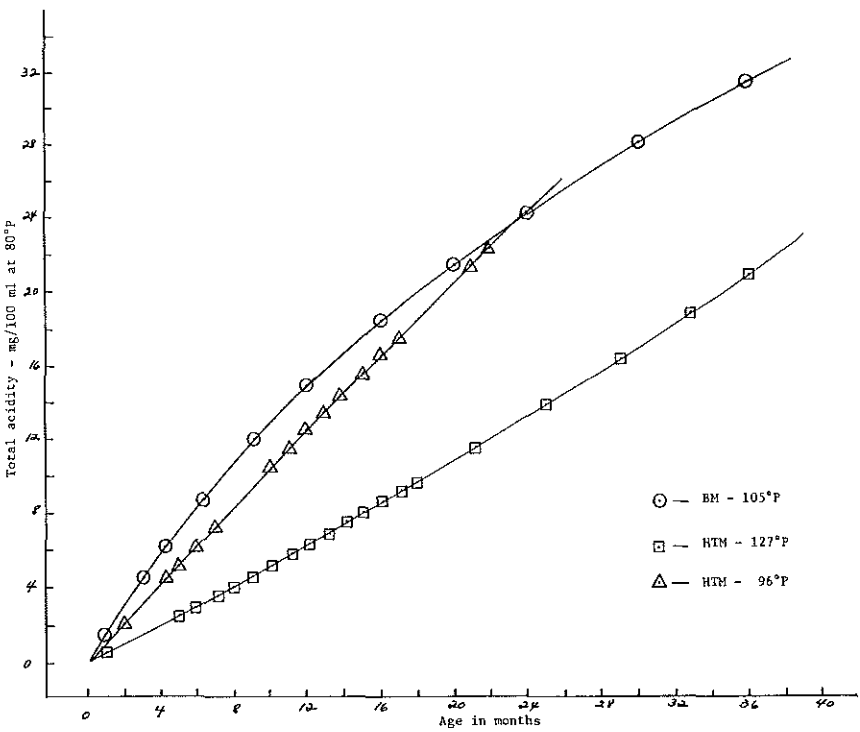

FIG. 7.—Changes in total acidity content of high-test and blackstrap molasses rums during aging.

acidity[4], 3 mg at the end of the first 6 months of aging, 6 mg during the first year, 7 during the second, and 9 during the third, for a total of 22 at the end of the 36-month maturing period. HTM rums 96° P showed an increase in total acidity of 7 mg at the end of the first 6 months of aging, 12 mg during the first year and 12 during the second, for a total of 24 at the end of the 24-month maturing period. HTM 96° P rum gained in 2 years twice the acids reported by the 127° P rum during the same period of aging. HTM rum 127° P took more than 1 year of aging to obtain the amount of acids reported by HTM rum 96° P in 2 years. In general, at the end of the 2-year maturing period, HTM rum 96° P reported an average of 1.7 more acids than 127° P rums.

When the HTM aging rum data were compared to the results of Brau and Camacho (3), it was found that initial content of total acids in the 105° P BM rum was about 10 times higher than that of HTM rums. The BM rums increased total acid content more rapidly than 96° P HTM rum, up to approximately 20 months of age, but at the end of the 24-month maturing period, 96° P HTM rum reported more total acidity than 105° P BM rum. Data suggest that the rate of maturation of rums in terms of acid gains is slower in the HTM rum than in the BM rums during the first 20 months of aging, but as the maturing period increases, the proof of the spirit predominates over the origin of the distillate as the determinating factor of acid gain during aging.

Esters, ethyl and methyl acetates (figures 8 and 9)

Esters are formed during aging mainly by the esterification of acids. Since their formation depends on acid concentration, it has been found that formation of esters lagged behind acid formation. Formation of esters in both 96° and 127° P rums showed a straight line development during aging. HTM rums 127° P, which started to age with 2 mg of ethyl acetate, gained one more miligram at the end of the first 6 months of aging and two more in the second half of the first year of maturing, seven at the end of the second year and three at the end of the 36-month aging period.

HTM rum 96° P, which started with 1 mg ethyl acetate, gained 2 more during the first 6 months of aging, two more at the end of the first year, and five more at the end of the 24-month maturing period. In general HTM rums 127° P reported 1.2 more ethyl acetate than HTM rum 96° P during the second year of maturing.

HTM rum 127° P showed an increase of methyl acetate of 1 mg during the first year and 1 during the second, but lost 1 during the third. HTM rum 96° P showed an increase of 1 mg during the first and 1 during the

[4]Total acidity is expressed as acetic acid, predominant analyzed (acid-base titration) acid in rum.

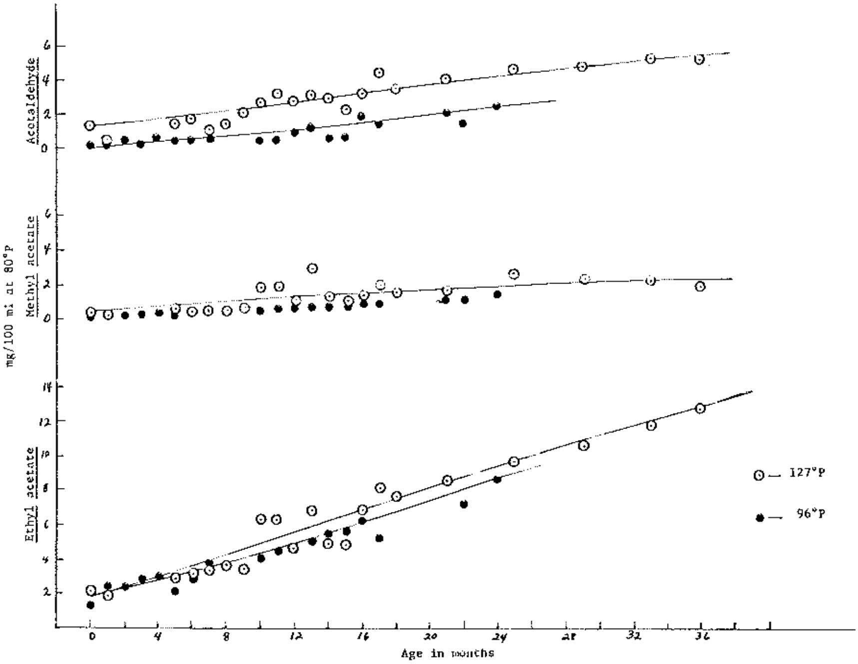

FIG. 8.—Changes in ethyl acetate, methyl acetate, and acetaldehyde of high-test molasses rums barreled at 96° and 127°P during aging.

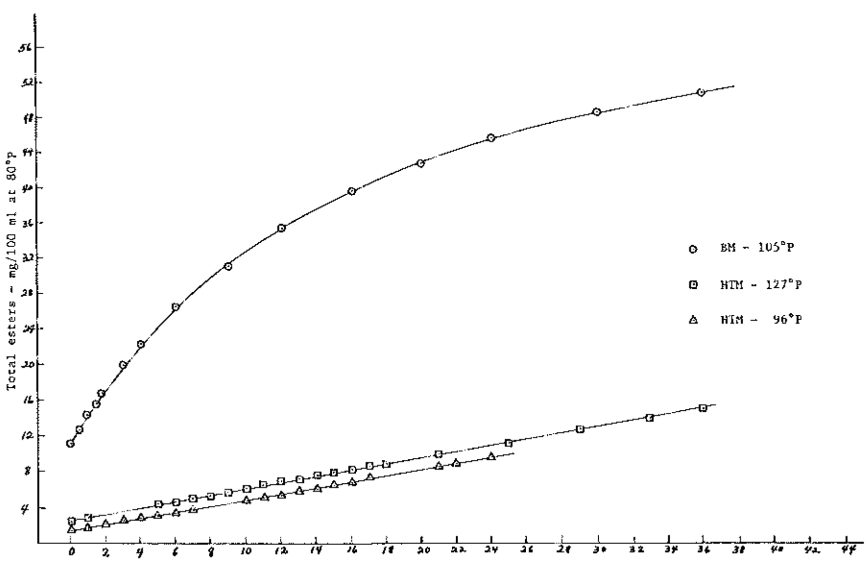

FIG. 9.—Changes in total esters content of high-test and blackstrap molasses rums during aging.

second. There was no significant difference in methyl acetate contents of aging HTM rums related to proof of the spirit. At the barrel level there is a slight difference favoring a larger increase of methyl acetate at 127° P HTM rum than at 96° P HTM rum at the end of the 24-month maturing period.

When HTM aging rums data were compared to Brau and Camacho's (3), it was found that initial content of total esters in the BM rum was 5 times greater than that of HTM rums. Data proved that the BM rum developed significantly more esters than HTM rums. The pattern of formation of total esters in the BM rum during aging followed the curve of a hyperbola, whereas HTM rum gains of esters followed a straight line development. Gains of esters are distributed more homogenously during aging of HTM rums, whereas in the BM rum they appear to form in larger quantities at the beginning of the maturing period. Since the initial concentration of acids in BM rums was significantly higher than that of the HTM rums, it is reasonable to observe an increase in the velocity of the esterification reactions of the BM rums.

Acetaldehyde and total aldehydes (figures 8 and 10)

Acetaldehyde is formed during aging. Because of its high volatility, part of it is lost by evaporation through the walls of the barrel, and the result is generally an increase in concentration during aging. Formation

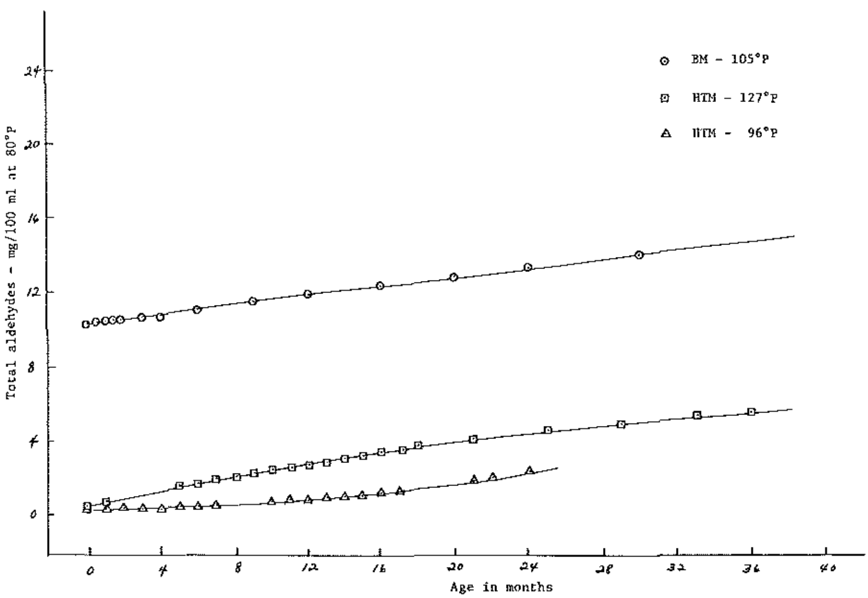

FIG. 10.—Changes in total aldehydes content of high-test and blackstrap molasses rums during aging.

of acetaldehyde during the 24- and 36-month maturing periods proceeded in a straight line development. HTM rums 127° P showed an increase of 2 mg during the first year, 2 during the second, and 1 during the third. HTM rum 96° P gained 1 mg acetaldehyde at the end of the first year of aging and 1.5 at the end of the 24-month maturing period. HTM rum 127° P gained 1.3 more acetaldehyde than HTM rum 96° P during the 2-year maturing period.

When HTM data was compared to BM data from Brau and Camacho (3) it was found that development of total aldehydes was similar in the 2 molasses substrates, although barreled BM spirits had 10 times more aldehydes than any of the HTM rums.

Fusel oil (figures 11 and 12)

The sum of the concentration of high molecular weight aliphatic alcohols is known as fusel oil. It has been reported that aging scarcely affects the original fusel oil content of barreled spirits and that apparent increases may result from the concentration caused by evaporation of water and ethyl alcohol. The propyl alcohol content of HTM rum 127° P remained unaffected during the first 2 years, but showed a significant increase of 1.7 times more during the third year; isoamyl alcohol showed an increase of 1 mg during the first year and insignificant increases dur-

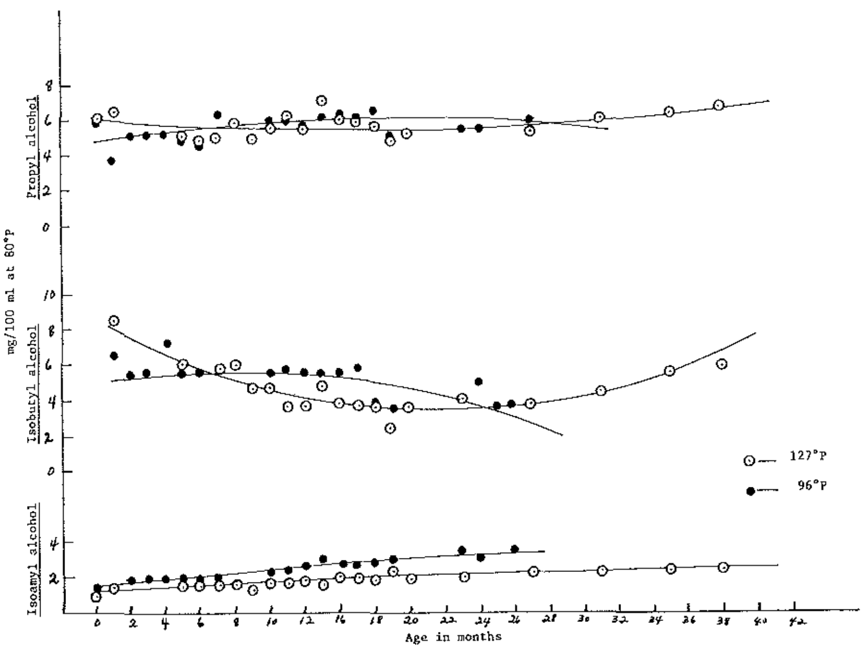

FIG. 11.—Changes in isoamyl, isobutyl and propyl alcohols of high-test molasses rums barreled at 96° and 127°P during aging.

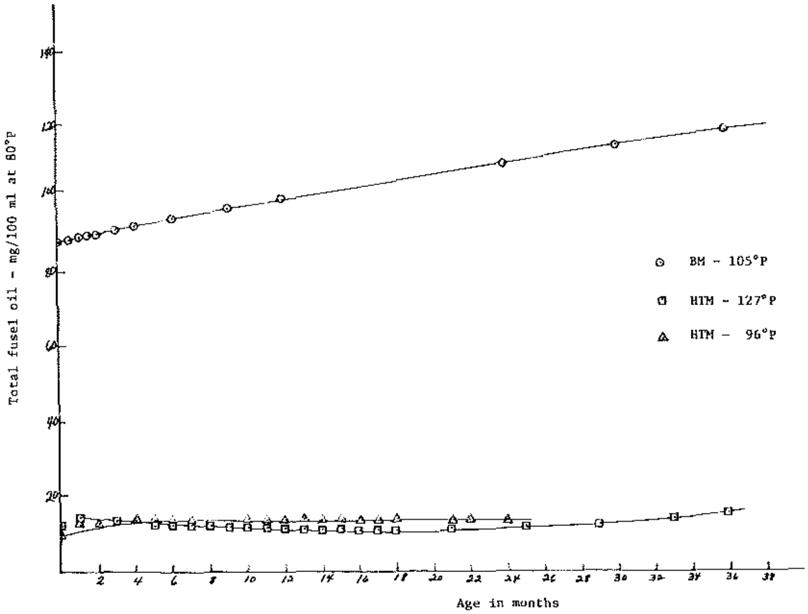

FIG. 12.—Changes in total fusel oil content of high-test and blackstrap molasses rums during aging.

ing the other 2 years. HTM rum 96° P content of propyl alcohol was found unaffected during the first year of maturing and increased insignificantly during the second year; isobutyl alcohol showed a significant increase of 3 mg at the end of the first year but lost 2 of them during the second year, for a balance of 1.6 more isobutyl alcohol gained at the end of the maturing period. Isoamyl alcohol showed an increase of 1 mg during the first year and one during the second.

The amount of fusel oil in the BM rum as reported by Brau and Camacho was nine times greater than that in the HTM rums, but in spite of this difference, similar trend of changes were observed in both of these aging distillates.

CONCLUSION

Development of maturity of HTM rums aged during 24- and 36-month maturing periods showed significant increases in color, total solids, tannins, total acids, ethyl and methyl acetates, acetaldehyde, and isobutyl and isoamyl alcohols; propyl alcohol remained relatively unaffected during the aging periods. HTM rums 96° P reported an average of 1.6 times more tannins and acids than HTM rums 127° P in the period from 1 to 2 years of aging, but gains in ethyl acetate and acetaldehyde were 1.2 times more at 127° P than at 96° P HTM rums; changes in methyl acetate, isobutyl and isoamyl alcohol contents were found relatively independent of the proof of the rum.

Increases in total solids and tannins in 96° P and 127° P HTM rums were distributed during the 24- and 36-month maturing periods following the curve of a hyperbola, which points to the extraction of limited quantities of wood material, the largest quantities being extracted early in the aging period. Increases in acids, ethyl and methyl acetates, acetaldehyde, and isobutyl and isoamyl alcohols were distributed more homogeneously throughout the maturing period as indicated by the straight line development of their changes.

A preliminary comparison of the development of the maturity of HTM and BM rums may indicate that during the first months of aging both substrates extracted equal quantities of tannins, independently of the sample proof, but as aging progressed, BM rums slowed down tannin extraction earlier than HTM rums. BM rums reported more acids than HTM rums until approximately 20 months of age, but from there on, HTM rums started to report larger contents of acids. The BM rum developed significantly more esters than HTM rums. Development of total aldehydes and changes of content of total fusel oil were similar in HTM and BM aging rums. The changes in total acids, total esters, total aldehydes and total fusel in HTM and BM rums during aging may have been affected by significantly larger differences among the initial concentrations of the evaluated samples.

An experiment on the aging of HTM and BM rums conducted under similar conditions of initial content of congeners as well as barreling proof, ambient conditions, type of barrel, barreled volume is in progress and results will be reported later.

RESUMEN

Envejecimiento de rones de mieles ricas

Se llevó a cabo un experimento de 2 y 3 años de duración sobre la maduración de aguardientes producidos de la fermentación de mieles ricas. En general se encontró que los destilados de mieles ricas presentaron aumentos significativos de contenidos en taninos, sólidos totales, ácidos totales, acetato de etilo, acetato de metilo, acetaldehído, alcohol isobutílico y alcohol isoamílico. El alcohol propílico se mantuvo inalterado durante el período. Los destilados embarrilados a 96° P arrojaron contenidos más altos en taninos, sólidos totales y ácidos totales que los destilados embarrilados a 127° P, pero los aumentos en acetato de etilo y acetaldehído resultaron más altos en los destilados embarrilados a 127° P. Los aumentos en acetato de metilo, alcohol isobutílico y alcohol isoamílico demostraron ser independientes del grado prueba del ron. Los aumentos en taninos y sólidos totales siguieron la curva de una hipérbola que señala hacia la extracción de una cantidad limitada de materia del barril. Los aumentos en acetato de etilo, acetato de metilo, acetaldehído, alcohol isobutílico y alcohol isoamílico se

desarrollaron en relación directa con la duración del envejecimiento y distribuidos uniformemente a lo largo del mismo.

Se realizó una comparación preliminar del desarrollo del envejecimiento de rones de mieles ricas y de rones de mieles finales. Se encontró que durante los primeros meses de envejecimiento los destilados de ambas materias primas extrajeron la misma cantidad de taninos, independientemente del grado prueba del destilado, pero a medida que se alargaba el período de maduración, se obtenían mayores cantidades de taninos en los rones de mieles ricas. Los rones de mieles finales demostraron mayor rapidez en la formación de ácidos en los primeros 20 meses de envejecimiento que los rones de mieles ricas, pero a medida que se alargaba el envejecimiento se favorecía la formación de mayor acidez en los rones de mieles ricas. Los rones de mieles finales presentaron concentraciones de ésteres totales mucho más altas que las de mieles ricas. Los cambios en concentración de aldehídos totales y de aceite de fusel fueron similares en los rones de ambas muestras de mieles. Se está realizando un experimento paralelo de envejecimiento de rones de mieles ricas y finales para comprobar, si algunas, diferencias en la maduración de los destilados de estas dos materias primas.

LITERATURE CITED

1. Arroyo, R., 1945. Studies on Rum, Agric. Exp. Stn., Univ. P. R., Res. Bull. 5: 1 138-70.
2. Boruff, C. and L. Rittschof, 1959. Effects of barreling proof on the aging of American whiskies, J. Agric. Food Chem., (9): 630-31.
3. Brau, H. and B. Camacho, 1960. Estudios sobre tecnología de ron, Mimeograph Publ., Agric. Exp. Stn., Univ. P. R., pp 31-43.
4. Liebmanm, A. J. and M. Rosenblatt, 1942. Changes in whisky while maturing; Ind. & Eng. Chem. 35 (9): 994-1,002.
5. Martínez, G. and N. Murphy. 1984. Congeners from high-test molasses alcoholic fermentation. J. Agric. Univ. P. R., 68 (1): 59-66.
6. Murphy, N., 1984. Fermentation of high-test molasses, J. Agric. Univ. P. R., 68 (1): 33-44.
7. Official Analytical Methods of the Rum Pilot Plant. 1969, Agric. Exp. Stn., Univ. P. R.
8. Ramírez, M., 1982. Characterization of slops of high-test molasses alcoholic fermentation, J. Agr. Univ. P R., 66 (3): 235-37
9. Spencer, G. and G. Meade, 1964. Cane Sugar Handbook, 9th ed, John Wiley & Sons, New York, pp 272-83.
10. Torres, Calixta S., 1973. Literature review of studies of natural rum aging, Rum Pilot Plant Report 2-73, Agric. Exp. Stn., Univ. P. R.