Congeners from High Test Molasses Alcoholic Fermentation[1]

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ABSTRACT

Distillates from fermented mashes of high test and blackstrap molasses were analyzed for congeners content. A product with more esters and less fusel oil, that appears convenient for high quality rum manufacturing, was obtained from the fermentation of high test molasses. These results suggest that high test molasses could be an alternative for the rum industry which may determine the viability of the local cane sugar industry.

INTRODUCTION

Blackstrap molasses, a by product from the sugar industry, is the principal raw material used to manufacture rum. The Puerto Rican sugar industry has declined continuously during the last decade. In some agricultural areas the sugar cane crop has been reduced drastically or is on its way to extinction. This is due to the drastic decrease in the international sugar prices: from a record price of 65 cents/pound in 1974, it dropped to eight cents in 1977 (2,7). From February to May, 1982 the U.S. prices have been between 11–12 cents per pound. During the same period the cost of the entire process from planting sugar cane to sugar extraction in the factory has increased significantly to levels in which sugar is produced at 28 cents per pound, making the enterprise unprofitable in Puerto Rico.

An alternative, that may viabilize sugar cane crop production and ensure raw material for the local rum industry is the production of high test molasses (HTM) parallel to or instead of granulated sugar.

HTM is a sugar cane syrup obtained by partial inversion of sucrose before final concentration of the clarified sugar cane juice, produced with higher sugar and lower ash content than blackstrap molasses. The production of such a material, probably on high demand from the rum industry, could be in the long run a better outlet for the local sugar cane crop. It will undoubtedly, constitute a profitable business if its fermentation can yield high quality rums efficiently and economically. It was found in this Station that slops from high test molasses reported significantly lower biological oxygen demand (BOD); thus less contaminant power than blackstrap molasses slops (13).

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At the beginning of the century some countries like Cuba (5) and Philippines (1) were interested in HTM production; lately other governments in India (3,4) and Brazil (6) and the United States (15) initiated programs in this field (16). Although much of the high test molasses produced was fermented for rum production, scarce information is available on the quality of the distillates obtained. It can be inferred that the differences in the composition of high test molasses and blackstrap molasses, as shown below (9),

Components	*Commercial high test molasses*	*Blackstrap molasses*
Specific gravity, °Bx	80–86°	86°
pH	5.0–5.7	5.6
Total sugars as invert	74–79%	57%
Invert sugar	50–60%	20%
Sucrose	12–26%	37%
Soluble solids, non sugar	6.0–7.5%	29%
Ash	2.2–3.0%	9%

could account for any differences in the quality of the distillates obtained as a result of their fermentation. In agreement with this line of thought the use of blackstrap molasses in the preparation of yeast seed for accelerating the fermentation of HTM (10) may also produce a different distillate.

In this paper we report the results of a comparative study on composition of distillates from high test and blackstrap molasses fermentations conducted at the Rum Pilot Plant.

MATERIALS AND METHODS

The study was initiated with two preliminary experiments on fermentation products of high test molasses manufactured at laboratory scale in this plant as compared with commercial blackstrap molasses samples. Fermented mashes were obtained following the usual yeast screening procedures of the Rum Pilot Plant (12) using only the PPR-80 yeast seed. After been distilled with a 40-plate fractional distilling column, products were analyzed by gas chromatography with the finger printing technique, in which only peak heights were recorded and measured. Preliminary identification of the peaks and quantitative analysis of components was not intended during these preliminary experiments. The results presented in table 1 and figure 1 justified running a similar experiment aimed at identifying and quantifying the components present.

The subsequent experiment used a HTM sample produced by enzy-

matic inversion at Guánica Sugar Mill during the 1981 sugar cane harvest (14). The blackstrap molasses sample was furnished by a local distillery. Details on fermentation procedures are described in a previous paper (10). Initial yeast seed with *Saccharomyces cerevisiae* PPR-80 strain was prepared by repeated aerobic transfers to nutrient molasses medium. Three different fermentation media were prepared as follows:

TABLE 1.—*Peak height in mm.*

Congeners	Experiment HTM	F-27 BM	Experiment HTM	F-28 BM
Acetaldehyde	1.26	t	1.82	t
Ethyl acetate	7.76	3.61	6.40	4.98
Propyl alcohol	5.99	6.98	3.75	6.76
Isobutyl alcohol	3.21	3.93	2.89	3.78
Isoamyl acetate	t	t	t	0.30
Butyl alcohol	t	0.40	t	0.40
Isoamyl alcohol	9.02	17.97	8.17	18.63

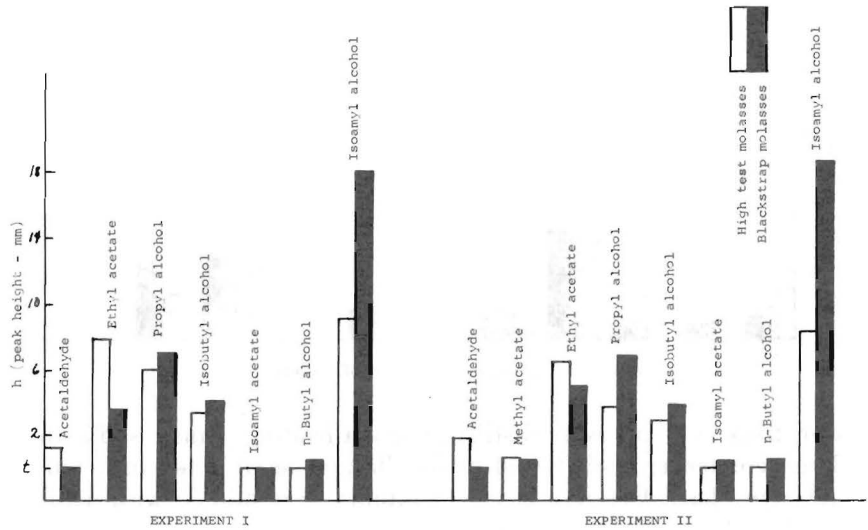

FIG. 1.—Congener content of distillates (previous work).

Sample	*Yeast inoculum*	*Plus*	*Fermentation mash*
Fermenter 1	2 L yeast grown in HTM at 17° Brix	+	14 L HTM mash at 17° Brix
Fermenter 2	2 L yeast grown in BM at 23° Brix	+	14 L HTM mash at 17° Brix
Fermenter 3	2 L yeast grown in BM at 23° Brix	+	14 L BM mash at 23° Brix

Initial sugar in the three fermenters was approximately 17 grams/100 ml; pH was adjusted to 4.8; ammonium sulfate was added in concentrations of 1.5 g/L to blackstrap molasses and 2.0 g/L in the case of high test molasses. Fermentation was allowed to continue up to 40 hours at room temperature, at which time it had stopped.

After completion of the fermentation, samples from each fermenter were distilled and analyzed for alcohol yield and congener content. For comparison purposes distillation was accomplished by two different methods.

A short method, as described in (11): 75 ml fermented mash were transferred to a 250-ml round bottom flask and diluted to 100 ml with

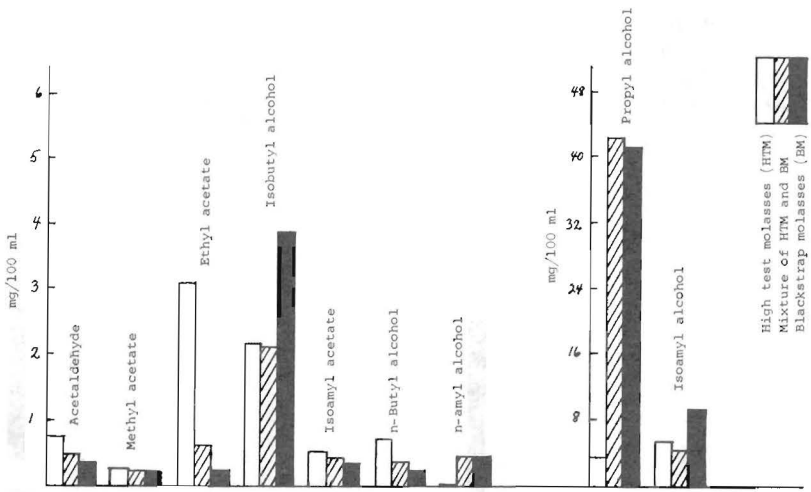

FIG. 2.—Congener content of distillates.

water; flask contents were distilled using a heating mantle and a 15-in column condenser until 60 ml of distillate were collected in a 100-ml volumetric flask. Before analyses, contents were diluted with distilled water to 100 ml.

A long method with a sample of 200 ml fermented mash diluted to 300 ml in a 500-ml round bottom flask and contents distilled through a 30-plate distillation column (fig. 2). Two 60-ml and one 50-ml fractions of distillate were collected. A composite distilled sample was prepared by mixing the three fractions and diluting them to 300 ml.

Products from the three fermented samples, distilled by both the short and the long method, were analyzed for alcohol by the refractive index method (11), and for congeners by gas chromatography.

The analysis of congeners was accomplished with a 5750 Hewlett

Packard gas chromatograph with a flame ionization detector.[3] A 18 ft × ⅛ in o.d. stainless steel column, packed with 60/80 mesh Chromosorb W-AW, coated with 5% Carbowax 20M was used. Other parameters were: 25 ml/min helium as carrier gas; initial temperature 50° C, programmed at 15° C/min rate until 150° C final temperature; injection port temperature 160° C, (8); 3 μl sample.

TABLE 2.—*Composition of the standard solution*

Congeners	mg/100 ml
Acetaldehyde	5.1
Methyl acetate	2.8
Ethyl acetate	9.0
Acetal	6.4
Propyl alcohol	14.5
Isobutyl alcohol	6.4
Isoamyl acetate	3.2
Butyl alcohol	3.4
Isoamyl alcohol	19.5
Amyl alcohol	4.9

Identification of congeners and their quantitative analysis was based on the reference solution described in table 2.

RESULTS AND DISCUSSION

Table 3 shows data on alcohol determination. No significant differences were observed in alcohol content between the two distillation methods: the short method resulted as accurate as the long method for the analysis of said component. It was found that more than 94% of the total alcohol yield is collected in the first fraction when the long distillation method is used. The first two fractions account for more than 99.9% of the total alcohol in the sample.

Also there were no significant differences in congener composition when the sample was distilled by the short and by the long method (table 4). For the purpose of the following observations, indiscriminate distillates (short or long methods) analyses of each fermenter were considered and recorded in table 4 and figure 2.

A comparison between fermented mashes (distillates) 1 and 3 (fig. 1 and 2) suggests that BM produced higher concentrations of propyl, isobutyl, isoamyl and n-amyl alcohols, but HTM produced only traces of

[3] Trade names in this publication are used only to provide specific information. Mention of a trade name does not constitute a warranty of equipment or materials by the Agricultural Experiment Station of the University of Puerto Rico, nor is this mention a statement of preference over other equipment or materials.

TABLE 3.—*Alcohol determination by two distillation methods (%/vol)*

Fermented mash	Method A	Method B			Mixture of 3 fractions	Absolute error	Relative error %
		Fraction 1	Fraction 2	Fraction 3			
1	9.03	17.51	0.51	0.28	9.01	0.02	0.22
2	8.87	16.94	0.73	0.28	8.84	0.03	0.34
3	8.96	16.94	1.01	0.36	8.98	0.02	0.22

TABLE 4.—*Congener content of distillates (mg/100 ml)*

Fermented mash	Distillation method	Acetal-dehyde	Methyl acetate	Ethyl acetate	Isobutyl alcohol	Isoamyl acetate	n-Butyl alcohol	n-Amyl alcohol	Propyl alcohol	Isoamyl alcohol
1 (HTM)	Method A	0.74	0.26	3.07	2.13	0.51	0.24	0	3.25	5.15
	Method B	0.69	0.21	1.26	2.30	0.51	0.75	0	3.65	5.25
2 (Mixture)	Method A	0.43	0.24	0.59	2.08	0.39	0.33	0.42	42.2	4.16
	Method B	0.67	0.24	0.98	2.37	0.19	0.20	0.67	48.7	5.02
3 (BM)	Method A	0.33	0.24	0.20	3.86	0.29	0.20	0.42	41.3	9.15
	Method B	0.44	0.24	0.23	4.49	0.39	0.23	0.67	49.3	10.91

n-amyl alcohol and higher concentrations of the esters ethyl and isoamyl acetate, acetaldehyde and n-butyl alcohol.

The very small amount of BM in fermenter 2 was enough to increase the amounts of propyl and n-amyl alcohols in distillates of HTM, and decrease amounts of ethyl and isoamyl acetates, acetaldehyde and n-butyl alcohol.

The concentration of methyl acetate ester seems to be independent of the molasses used. Acetal was obtained only as traces in all three fermented mashes, suggesting that its concentration does not depend on the type of the molasses used.

These results agreed with data of the two preliminary experiments conducted at this Plant.

It can be concluded that high test molasses competes favorably with blackstrap molasses, as a raw material for the rum industry in terms of alcohol yield and congener composition of the distillates.

RESUMEN

En la Planta Piloto del Ron se llevaron a cabo fermentaciones usando como materia prima miel rica, miel final y mezclas de ambas. Luego se determinó el alcohol producido y se evaluaron los congéneres presentes. Un destilado con mayor proporción de ésteres y menor proporción de fusel, ambas ventajas para la industria del ron, se obtuvo de la batición[4] fermentada de mieles ricas.

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