THE COMPOSITION OF FLORIDA CITRUS MOLASSES[1]

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Citrus molasses is a comparatively new product. Although information has been available on the composition of the press juice from which it is made, little has been published on the composition of the molasses itself. It is the purpose of this paper to present data obtained in chemical analyses of 13 samples of citrus molasses.

Citrus molasses is produced from the waste peel, rag, and seeds from the citrus canneries. The waste is first ground with a hammer mill into pieces about a quarter of an inch in diameter. Lime is added to neutralize the acidity, react with the pectin, and facilitate pressing and drying. The ground peel is passed through a pug mill in which it is kept in constant agitation for about 10 minutes or is placed in bins for 30 to 45 minutes to permit the lime to react. In areas where fuel is cheap the peel may be passed directly to the driers. In Florida where fuel costs are an important factor, as much of the liquid as possible is first removed by pressing and the pulp then passed to steam-heated or direct-fired rotary driers. The removed liquid, or press juice, is concentrated in multiple-effect evaporators, having two, three, or four effects and sometimes having a finishing pan. The juice has originally a soluble solids content of from 6 to 11 percent, depending on the nature of the fruit and method of handling the peel. For instance, the value will be lower if water has been used in transporting the peel or if a lime slurry has been used instead of dry lime. In the evaporators the soluble solids content is increased to about 73 percent. The temperatures used range from 245° to 135° F. and naturally vary with the type and the number of effects.

Both the dried pulp and molasses are used extensively as feeds. Citrus molasses is also used in the production of alcohol (12). Several studies have been reported on the feeding value and chemical composition of dried citrus pulp (1, 5, 6, 7, 8, 9, 10, 12, 13). Becker, Arnold, Davis, and Fouts (3 and 4) estimated 1.4 percent digestible crude protein and 56.7 percent total digestible nutrients in citrus molasses, based on 69.9 percent dry matter. These authors also reported 3 to 5 percent each of crude protein and ash and the absence of crude fiber. The manufacture of dried pulp and molasses provides a complete answer to the disposal problem of citrus peel in that all the organic matter is retained and converted to useful products.

Table I gives information on the production in Florida of dried citrus feed and molasses. It will be noted that the ratio of citrus molasses to dried pulp has been steadily increasing. In general, the mills have been equipped first for the

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production of dried pulp and the molasses units have been added later. A few mills still have no evaporators and the press juice is discarded.

Experimental

Samples of freshly manufactured citrus molasses were collected at intervals from the early part to well past the middle of the 1947-48 citrus canning season from eight feed and molasses plants in Florida. The samples were transported directly to the laboratory, being placed in a refrigerator at 350° F. within 3 days of manufacture. Portions were drawn from cold storage as needed for analysis, not more than two samples were taken from a single evaporator.

Official methods of analyses (2) were used in the determination of total solids, crude protein (N x 6.25), pectin (alcohol precipitate), ash, total acidity (calculated as citric acid), volatile acidity (calculated as acetic acid), calcium in ash, and magnesium in ash. Total sugars, nonreducing sugars, and reducing sugars were determined by the Munson-Walker gravimetric method and all reported as invert sugars. Overnight acid inversion was used. pH was determined with a glass electrode; degrees Brix with an Abbe type refractometer and by diluting with an equal weight of water and determining density with a spindle; color by comparison with Maerz and Paul color charts; and viscosity with a Stormer viscosimeter standardized with a Bureau of Standards reference fluid having a viscosity of 1282 centerpoises.

Results

The results of the analyses are given in Tables II and III. Samples Nos. 1, 4, 5, 6, 10, 11, and 12 were from plants with quadruple-effect evaporators having finishing pans; samples Nos. 2, 3, 7, 9, and 13 were from plants with triple-effect evaporators; and sample No. 8 was from a plant with a two-stage evaporator in which the first effect was the direct-fired spray type and the second of conventional design. Sample No. 4 was made from orange peel only; all the others were made from a mixture of grapefruit and orange peel.

Concentration. The results permit a comparison of the degrees Brix as estimated by the refractometer, spindle, and drying methods.

TABLE I

Production of Dried Citrus Pulp and Citrus Molasses in Florida

Season	*Dried Citrus Pulp*	*Citrus Molasses*
1940-41	32,730 tons	0
1941-42	29,696 tons	2,500[2]
1942-43	47,376 tons	5,700[2]
1943-44	67,130 tons	14,496 tons
1944-45	68,724 tons	19,260 tons
1945-46	108,470 tons	44,168 tons
1946-47	96,914 tons	55,811 tons
1947-48	154,181 tons[1]	65,887 tons[1]

Data obtained from Citrus Processors Association, Inc., Tampa, Florida.

[1] Tentative.

[2] Data from Office of Supply, War Food Administration.

The refractometer method, the one most generally used, indicated concentrations from 64.44 to 74.52 degrees Brix, with an average value of 71.37. It is believed that the lower values were largely due to the method of sampling in that samples of fresh material were taken and lots were generally blended later to the desired strength.

The spindle method of estimating concentration provides a rapid procedure when a refractometer is not available. The molasses is too thick for a direct reading; so it is diluted with an equal weight of water, the density determined corrections applied, and the result multiplied by two. The average value obtained was 72.28 degrees Brix, about 0.9 degrees higher than by the refractometer method.

In the third method of estimating concentration the samples were dried on pumice stone at 70° C. under vacuum. This method gave values averaging 70.43 percent total solids, or about 1 percent below those obtained with the refractometer. Any of the three methods of estimating concentration is suitable; but it should not be expected that identical values be obtained.

Sugars. The values for total sugars, reducing sugars, and nonreducing sugars show some variations, but these are to be expected with this type of product. The sugars averaged 59.8 percent of the total solids and ranged from 47.8 to 65.4 percent. With 9 of the 13 samples the percentage of sugars in the total solids was within the range of 55 to 65 percent. To obtain information on changes in sugars during concentration, 25 gallons of press juice were brought to the laboratory and concentrated under atmospheric conditions in a steam-jacketed kettle. Before concentration the Brix was 9.3 degrees, the reducing sugars 2.94 percent, and the total sugars 5.64 percent. After concentration the corresponding values were 73.86 degrees, 23.74 percent, and 44.55 percent, respectively. Since the ratios of these constituents were nearly the same after concentration as before, it was concluded that the sugars change very little during the process. It is believed that the conditions in the laboratory were as severe as those encountered in commercial plants.

Protein. The crude protein values ranged from 3.35 to 4.15 percent. While the amount present is significant, molasses must be classed as a low protein material.

Pectin. Pectin determinations by the alcohol precipitation method gave values ranging from 0.80 to 1.59 percent. These quantities of pectin probably contribute materially to the viscosity of the molasses. An effort was made to determine pectin acid by the official method but light-colored precipitates were never obtained and the values are not reported.

Acidity. Total acidity and pH are under the control of the operator by varying the amount of lime added. It is evident that most of the original acidity in the waste peel and pulp had been neutralized. The volatile acidity, as expected, was reduced to very low values by the concentration process.

Ash. The ash is due largely to the addition of lime to the peel and this is reflected in the high calcium values. Some magnesium was also found. Both of these elements are of value in the compounding of feeds.

Color. Most of the samples were quite dark in color, being brown to dark brown. Three of the samples, however, Nos. 3, 7, and 13, were lighter. The

TABLE II

COMPOSITION OF CITRUS MOLASSES

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	Ave.
Made	10/21/47	11/13/47	11/24/47	11/25/47	12/15/47	12/18/47	12/18/47	1/30/48	2/24/48	2/24/48	2/25/48	2/26/48	2/27/48	
° Brix (refr.)	71.64	71.48	64.44	70.98	71.42	72.72	69.34	72.02	71.46	71.89	71.45	74.40	74.52	71.37
° Brix (spindle)	70.46	73.02	64.25	73.41	72.24	73.72	70.04	72.09	73.46	73.55	72.99	75.52	74.94	72.28
Total Solids %	71.05	70.04	63.85	70.05	69.25	70.90	68.80	71.57	70.78	70.69	70.75	73.66	74.14	70.43
Volatile Matter %	28.95	29.96	36.15	29.95	30.75	29.10	31.20	28.43	29.22	29.31	29.25	26.34	25.86	29.57
Total Sugar %	46.50	41.58	39.60	44.68	33.10	46.56	44.83	38.52	42.77	41.04	37.45	42.13	46.06	42.09
Reducing Sugar %	19.66	19.46	20.49	22.66	16.88	23.62	24.98	25.85	25.87	23.65	22.71	21.83	24.01	22.44
Non-red. Sugar %	26.84	22.12	19.11	22.02	16.22	22.94	19.85	12.67	16.90	17.39	14.74	20.30	22.05	19.65
Protein, crude % (N x 6.25)	3.93	3.80	3.35	3.54	3.85	4.00	3.71	4.14	3.65	3.76	3.70	3.91	4.15	3.81
Pectin % (alc. ppt.)	0.91	0.99	1.05	1.19	1.21	1.59	1.25	0.97	0.80	1.08	1.09	0.99	0.80	1.07
pH	5.7	4.5	4.6	3.9	4.1	3.6	4.1	4.1	5.4	5.6	5.7	5.6	4.1	4.68
Total Acidity as Citric %	0.56	0.51	0.58	0.94	0.66	0.81	0.74	1.20	0.24	0.26	0.25	0.34	1.19	0.64
Volatile Acidity as Acetic %	0.02	0.02	0.04	0.06	0.07	0.09	0.04	0.17	0.02	0.04	0.05	0.02	0.05	0.053
Ash %	4.43	5.11	4.23	5.07	5.00	5.25	5.08	5.81	4.51	4.52	4.42	4.05	4.69	4.77

TABLE II–(Continued)
COMPOSITION OF CITRUS MOLASSES

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13	Ave.
Ca in ash %	24.6	30.7	29.5	28.9	33.4	28.4	27.4	34.5	34.1	27.4	28.6	28.2	32.2	29.84
Mg. in ash %	2.4	1.8	2.7	2.2	2.1	2.2	2.3	1.7	2.3	2.0	1.9	2.0	2.2	2.14
Color (M&P)	7-C-12	6-B-12	9-1-5	6-A-12	5-B-12	7-L-12	10-1-6	8-L-6	7-A-12	7-H-12	7-A-12	7-A-12	9-1-8	

TABLE III

VISCOSITY OF CITRUS MOLASSES

CENTIPOISES

Sample No.	1	2	3	4	5	6	7	8	9	10	11	12	13
77° F.	892		410		2320	4250	1445		4250			8030	5700
86° F.	606	4800	321	1471	1382	2800	1070	2441	2500	1659	2242	4820	3391
95° F.	446	3120	250	1026	891	1918	750	1480	1640	1160	1460	3210	2140
104° F.	321	2020	205	722	677	1356	553	963	1160	838	1070	2195	1460
113° F.	250	1440	169	538	500	1025	418	748	820	624	767	1532	1019
122° F.	209	1123	148	420	374	787	338	570	624	475	577	1107	748
131° F.	178	829	130	321	294	617	268	428	467	378	445	820	562
140° F.	152	642	121	252	246	467	216	334	357	303	350	625	432
149° F.	134	500	114	214	214	374	189	260	294	253	285	507	330
158° F.	121	407	103	187	182	312	164	214	250	223	243	407	267
167° F.	112	353	98	168	160	271	157	193	223	198	224	342	223
176° F.	107	312	98	183	157	241	150	169	205	187	214	307	196

amount of suspended matter and degree of dispersion may be the principal factors in these differences in color. The small particles of pulp darken very little during the concentration process. The pH and ash values were in the same range and this ruled out the possibility of differences in degree of liming. Samples Nos. 3 and 7 were below the average in concentration, and sample No. 13 above the average.

Viscosity. The viscosity values (Table III) are of interest in devising means and equipment for handling the citrus molasses. Values were obtained over the range of 77° to 176° F.; but no values are reported for temperatures lower than 77° F. because the instrument is not well-suited to solutions of the thickness encountered at those temperatures. As would be expected, the viscosity of each sample decreased rapidly with increase in temperature, but there was considerable variation among the samples. Some of this variation was due to the degree of concentration, sample No. 3 being the least concentrated as well as the least viscous. But since different samples of substantially the same concentration also showed substantial variations, probably the condition of the fruit, variety, time of the season, and method of preparation also affected the viscosity.

Discussion

In comparing the values obtained with those which Nolte, von Loesecke, and Pulley (12) obtained with citrus press juice, it is noted that the sugars constituted a smaller proportion of the total solids in the citrus molasses examined. The results of Nolte et al indicated 74 percent of the solids in the press juice to be sugar. Recently in connection with investigations on feed yeast, numerous analyses were made on citrus press juice. Occasionally percentages of 75 percent were obtained; but usually the values ranged from 50 to 70 percent. When the lowest values were encountered it was thought probable that there had been some loss of sugars by fermentation in the peel bins or during storage of the press juice. Protein values of the press juice were about in the same proportion as in the molasses; pectin values were smaller with citrus molasses, possibly because of the adverse effect of the heating during concentration. Fixed acidity was somewhat lower with the molasses, and as would be expected, tests for volatile citrus peel oils in the molasses samples did not reveal detectable quantities by the usual methods.

Summary

The chemical analyses of 13 samples of citrus molasses are presented. The average values obtained were: 71.37 degrees Brix by refractometer, 72.28 degrees Brix by spindle; 70.43 percent total solids; 42.09 percent total sugars; 22.44 percent reducing sugars; 19.65 percent nonreducing sugars; 3.81 percent protein; 1.07 percent pectin (alcohol precipitate); pH 4.68; 0.64 percent total acidity as citric acid; 0.053 percent volatile acidity as acetic acid; 4.77 percent ash; 29.84 percent calcium in ash; and 2.14 percent magnesium in ash. Viscosities at temperatures ranging from 77° to 176° F. and Maerz and Paul color values are also given.

The values obtained are in general agreement with those calculated from other data on the composition of citrus press juice from which the molasses is made. The material is high in carbohydrates and contains substantial quantities of crude protein and ash. Calcium

comprises a major portion of the ash. The citrus molasses is similar in composition to blackstrap molasses made from cane and finds similar uses, particularly in the compounding of mixed feeds.

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