tracted as in the case of the Elderberry, and added to a lime guava base. The wine resulting from this mixture was a light red, light bodied wine resembling a Claret. Varying concentrations of Antidesma juice were tried but anything beyond a 10 or 12% content was found to be too astringent and bitter for general acceptance.

The last type of fruit to be used as raw material for wines was the Malpighia or Barbados Cherry. Like so many other fruit, the cherry by itself gave a very harsh product but upon addition of lime juice and subsequent thinning with water a highly aromatic, smooth wine of a pale amber color was obtained. It was deemed fit for consumption shortly after bottling but did improve very much upon aging, it has been found to be extremely stable in clarity and color. The fermentation itself progressed smoothly with no particular need for aeration.

These tropical fruit wines have all been shown to have a wide acceptance. Taste tests covering a wide range of tasters with varied wine experiences have shown the flavor and appearance to be a good compromise between many characteristics that are usually either enthusiastically accepted or flatly rejected.

Not all of the available fruits have been tested, of course. Of these that have been tested, a red wine and a white wine of the guava-lime-elderberry and the guava-lime respectively seem to have the greatest promise commercially. The raw materials are immediately available and of a price that should easily allow competition with common market wines.

MATURITY CHANGES IN PINEAPPLE ORANGES AND THEIR EFFECT ON PROCESSED FROZEN CONCENTRATE[1]

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Maturity changes in citrus fruits have been studied from the standpoint of seasonal variations in soluble solids, acid, texture, color of both rind and juice, vitamin C, flavor, and in many other factors. However, total soluble solids/acid ratio is accepted by the citrus industry as one standard of maturity for oranges, tangerines, and grapefruit. Part of the Federal and State specifications for wholesome citrus juices and concentrates are based upon this soluble solids/acid ratio. The Florida Citrus Code (3) requires that frozen concentrated fresh orange juice be made from juice having a minimum ratio of eleven to one as evidence of ripeness and sets a maximum ratio of nineteen to one.

The question has arisen as to whether there is a ratio between the minimum and maximum ratios where the water-soluble pectic fraction, the constituent producing the "cloud" of the juice is highest and where pectinesterase activity, the enzyme causing the formation of low-methoxyl pectin which results in gelation and clarification, is lowest. Increased emphasis on clarification in reconstituted juice and gelation in frozen citrus concentrate has intensified the need for additional information concerning these undesirable changes.

During the past several years several investigators (1, 7, 8, 10) have used heat to inactivate the enzyme, pectinesterase, to protect the water-soluble pectin in concentrate from demethylation and to stabilize the "cloud." Last year Huggart (5) reported that the stabilization of citrus concentrates to enzymic clarification and gelation can be obtained by high concentration without heat.

In 1934 Gaddum (4) presented data showing the effect of maturity on two pectic fractions from albedo, pulp, and juice of Valencia oranges. Since Gaddum's early work pectins can now be characterized into additional fractions and the effect of pectinesterase on pectin is better understood. This investigation was undertaken to determine the effect of fruit maturity, as indicated by soluble solids/acid ratio, on the pectic substances and pectinesterase activity in the component parts of Pineapple oranges, picked over a period of five months. Frozen concentrates were made monthly from

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2/Florida Citrus Experiment Station.

3/Florida Citrus Commission.

this fruit to determine changes in pectic substances and pectinesterase that may occur during processing and storage.

Experimental Procedure

Selection of Fruit and Preparation of Samples. Nine Citra Pineapple orange trees were selected from Block II at the Citrus Experiment Station and reserved for this maturity study. These trees received normal fertilizer and spray practices. A total of 288 oranges, 32 from each tree, were picked from the nine trees each month for the experimental packs and analyses. Four fruit were picked from both the inside and the outside of each tree from top to bottom and from four sides.

The oranges were washed, wiped dry, and peeled by hand to remove the flavedo and albedo which comprise the peel. The peeled fruit was halved and passed through a Food Machinery finisher, Model 35, fitted with a 0.020 inch screen and having the pressure head set loosely. Each month the resulting juice was concentrated to 55° Brix and cut-back to 42° Brix concentrate with pulpy juice which was prepared by passing the residue, remaining from the finishing operation above, through a 1/8 (0.125) inch screen. The 42° Brix concentrate was filled into 6 oz. cans, vacuum sealed, and placed in –8° F. storage.

The peel was prepared for analyses by grinding it in a food chopper so that composite samples could be secured. The pulp (segment membrane, juice sacs, and some broken seeds) was comminuted in an Osterizer and separated from excess juice by centrifugation. To 50 g. of ground peel and to 50 g. pulp were added 150 g. and 100 g. of water, respectively, which was sufficient to cover the samples. These mixtures as well as juice to evaporator, cut-back juice, and 55° and 42° Brix concentrates were each comminuted in an Osterizer for 3 min. and samples taken for analyses. The centrifuged juice consisted of juice which passed the 0.020 inch screen and was then centrifuged to remove the water-insoluble solids.

Analytical Methods. Pectinesterase activity was assayed essentially by the procedure of MacDonell, Jansen, and Lineweaver (6), using a Beckman Model K Automatic Titrator. Pectinesterase units (PE.u.) were expressed as the milliequivalents of ester hydrolyzed per minute per gram of total solids. These were multiplied by 1000 for easy interpretation.

The pectic substances after being divided into three groups on the basis of their solubility at room temperature in water, in sodium metaphosphate, and in sodium hydroxide were determined by the rapid colorimetric method of Dietz and Rouse (2).

Total solids determinations were made by removing excess water in a drying oven at 80° C. for 2 hr. and finally drying at 70° C. in a vacuum oven for 12 hr.

Soluble solids were determined by a Bausch and Lomb refractometer at 28° C. and expressed as degrees Brix.

Pulp content was estimated by centrifuging a 50 ml. sample of juice at 1600 r.p.m. for 15 min. in a Size 1, Type SB International Centrifuge.

Experimental Results and Discussion

Maturity Changes in Pineapple Oranges. General analyses of Pineapple oranges showing changes in composition over a period of five months are presented in Table 1. Juice from the oranges picked in December had a Brix/acid ratio of 10.5, whereas the fruit picked in April had a ratio of 18.8. As the ratio increased the total solids, soluble solids, and pH increased as expected with a percentage decrease of citric acid. The pulp content

Table 1

Initial analyses of Pineapple orange juices showing maturity changes over a five month period from December 1952 through April 1953

Date fruit picked	Total solids %	°Brix by refract. at 28°C.	Acid as citric-%	Maturity Brix/acid ratio	pH	Pulp - % by volume Evaporator juice	Pulp - % by volume Cut-back juice
12-11-52	11.3	11.1	1.06	10.5	3.6	10.0	36.0
1-13-53	11.8	12.0	1.00	12.0	3.7	13.0	45.0
2-12-53	13.0	13.0	0.95	13.7	3.8	13.0	48.0
3-12-53	12.7	13.0	0.82	15.9	4.0	12.0	45.0
4-14-53	13.6	13.7	0.73	18.8	4.0	13.0	44.0

of the 0.020 inch screened juices varied slightly from 10 to 13% and the pulpy cut-back juices varied from 36 to 48% pulp by volume.

Data presented in Table 2 show the effect of maturity on pectinesterase activity and on the pectic fractions in peel, pulp, cut-back juice, evaporator juice, and centrifuged juice on a dry solids basis. Since pectinesterase activity is associated with the solid particle, the centrifuged juice contained very little activity.

Enzymic activity was highest in the pulp and the general trend in the component parts, except for the centrifuged juice, was for the activity to increase as the Brix/acid ratio increased from 10.5 to 15.9, but when the ratio increased to 18.8 in April the pectinesterase activity definitely decreased in all component parts. The cut-back juice was next highest in activity followed by the peel and juice to the evaporator.

From the data in Table 2, the percentage of total pectin increased slightly and then decreased in each component with increased Brix/acid ratio except for the centrifuged juice. In the case of the centrifuged juice, the water-insoluble solids were removed leaving only the water-soluble pectic fraction, which remained constant throughout the maturity study. Also as the fruit matured, the sodium hydroxide-soluble fraction, protopectin, decreased in all of the components. The trend noted was that the water-soluble pectic fraction decreased with maturity and the polyphosphate pectic fraction increased during the first four months of the study and decreased the last month. It is of interest to note that as the polyphosphate pectic fraction decreased, when the ratio reached 18.8, so did the pectinesterase activity.

Processing and Storage Changes. Processing and storage changes in both pectinesterase activity and pectic fractions are shown in detail in tabular form and only the more significant features will be briefly discussed.

The results in Table 3, showing the effect of processing and 24 hr. storage at 80° F. on pectinesterase activity, further confirmed the data presented last year by Rouse (9), that there was a decrease in activity when the product was held at room temperature. The data indicate a lessening in activity during processing

Table 2
Effect of maturity on pectinesterase activity and on pectic fractions in component parts of Pineapple oranges and in juices used to process 42°Brix concentrates

Maturity Brix/acid ratio	Component part	Total solids %	(PE.u.)g. dry basis X 1000	Pectin as anhydrogalacturonic acid dry basis: H_2O-sol. %	$(NaPO_3)_n$-sol. %	NaOH-sol. %	Total %
10.5	Peel	30.1	50.8	1.54	6.17	9.75	17.46
12.0	"	27.9	145.7	1.95	7.60	8.87	18.42
13.7	"	27.1	120.8	1.19	7.63	9.29	18.11
15.9	"	25.8	122.1	0.39	11.66	7.38	19.43
18.8	"	27.2	90.1	0.76	8.10	7.46	16.32
10.5	Pulp	14.4	322.9	0.90	1.90	4.91	7.71
12.0	"	15.0	302.1	1.19	1.94	4.95	8.08
13.7	"	15.4	325.9	1.08	2.34	3.66	7.08
15.9	"	15.4	439.5	1.34	2.83	3.09	7.26
18.8	"	16.1	327.6	0.43	2.21	2.88	5.52
10.5	Cut-back juice	12.6	126.3	1.15	0.90	2.28	4.33
12.0	" "	13.3	160.8	1.14	0.95	2.27	4.36
13.7	" "	13.8	180.8	1.14	1.15	1.82	4.11
15.9	" "	13.8	194.4	1.02	1.23	1.65	3.90
18.8	" "	14.5	97.7	0.83	0.92	1.27	3.02
10.5	Evaporator juice	11.3	17.1	0.23	0.13	0.28	0.64
12.0	" "	11.8	18.9	0.28	0.15	0.25	0.68
13.7	" "	13.0	19.8	0.23	0.20	0.26	0.69
15.9	" "	12.7	19.2	0.19	0.19	0.23	0.61
18.8	" "	13.6	14.3	0.20	0.16	0.20	0.56
10.5	Centrifuged juice	10.6	2.2	0.21	--	--	0.21
12.0	" "	11.6	1.1	0.21	--	--	0.21
13.7	" "	12.7	0.8	0.23	--	--	0.23
15.9	" "	12.5	0.8	0.20	--	--	0.20
18.8	" "	13.5	0.6	0.19	--	--	0.19

Table 3.

Effect of processing and short-term storage on pectinesterase activity on dry solids basis in Pineapple orange juices and concentrates prepared during the maturity study

Maturity Brix/acid ratio	Juice to evaporator	55°Brix conc. from evaporator	42°Brix concentrate	
			Initial	After 24 hr. at 80°F.
	(PE.u.)g. x 1000	(PE.u.)g. x 1000	(PE.u.)g. x 1000	(PE.u.)g. x 1000
10.5	17.1	14.7	27.9	25.8
12.0	18.9	17.8	41.5	31.0
13.7	19.8	18.2	42.7	33.8
15.9	19.2	16.6	39.1	34.3
18.8	14.3	12.2	33.9	27.1

and an apparent decrease of activity in 42° Brix concentrates after 24 hr. storage at 80° F.

The pectic fractions expressed as percentage of total pectin, in evaporator juices and pulpy cut-back juices used in preparing the 42° Brix concentrates during the maturity study are presented in Table 4. Two significant facts are indicated: (a) as the Brix/acid ratio increased the percentage of water-soluble pectin remained practically constant in the two groups of juices, the polyphosphate-soluble pectin increased, and the sodium hydroxide-soluble pectin decreased; (b) the percentage of water-soluble pectin in juices to the evaporator, expressed as percentage of total pectin, was higher than that found in the cut-back juices. This would mean that if the cloud of a reconstituted citrus juice results from the water-soluble pectin in the evaporator juice, then it should be protected during evaporation from demethylation caused by pectinesterase.

The average results of five packs showing the changes in pectic substances, expressed as the percentage of total pectin, during processing and short-term storage of 42° *Brix Pineapple* orange concentrates are presented in Table 5. For example, of the total pectin in five juices to the evaporator, there was 35.4% water-soluble, 26.3% polyphosphate-soluble, and 38.3% sodium hydroxide-soluble. After the five juices were each concentrated to 55° Brix and the results averaged, the water-soluble fraction decreased to 23.2%, the polyphosphate-soluble fraction increased to 38.9%, and the sodium hydroxide-soluble fraction remained constant. Also shown are the 42° Brix concentrates with the average changes in pectic substances of five packs, initially and after 24 hr. storage at 80° F. The pectic changes taking place during storage are similar to those that take place during processing.

Data in Table 6 show the sum of both the water and polyphosphate-soluble pectins on wet basis in 42° Brix concentrates, initially

Table 4

Pectic changes in Pineapple orange juices and pulpy cut-back juices used in preparing 42°Brix concentrates during the maturity study

Type of juice	Maturity Brix/acid ratio	Percentage of total pectin		
		H_2O-sol. %	$(NaPO_3)_n$-sol. %	NaOH-sol. %
Juice to evaporator	10.5	35.9	20.3	43.8
" " "	12.0	41.2	22.1	36.7
" " "	13.7	33.3	29.0	37.7
" " "	15.9	31.1	31.2	37.7
" " "	18.8	35.7	28.6	35.7
Cut-back juice	10.5	26.6	20.8	52.6
" " "	12.0	26.1	21.8	52.1
" " "	13.7	27.7	28.0	44.3
" " "	15.9	26.2	31.5	42.3
" " "	18.8	27.5	30.5	42.0

Table 5

Changes in pectic substances during processing and short-term storage of 42°Brix Pineapple orange concentrates

Type of juice or concentrate	Average results of five packs — Percentage of total pectin		
	H_2O-sol. %	$(NaPO_3)_n$-sol. %	NaOH-sol. %
Juice to evaporator	35.4	26.3	38.3
55°Brix conc. from evaporator	25.9	38.0	36.1
Pulpy cut-back juice	26.8	26.5	46.7
42°Brix conc., initial	26.7	35.7	37.6
42°Brix conc., after 24 hr. at 80°F.	8.1	55.0	36.9

and after 24 hr. storage at 80° F. The sum of these two pectic fractions remained virtually constant, but as shown in Table 5 there was a decrease in the water-soluble fraction and an increase in the polyphosphate-soluble fraction during storage of the concentrates. In the initial 42° Brix concentrates, there was no clarification and very slight gelation but after storage at 80° F. for 24 hr. extreme clarification and semi-gels appeared in all five samples packed monthly from December 11, 1952 to April 14, 1953.

Summary

Pineapple oranges were harvested once a month for a duration of five months, beginning with a low Brix/acid ratio of 10.5 and ending with a high Brix/acid ratio of 18.8, to study the changes in pectinesterase activity and pectic substances.

The trend was for the pectinesterase activity to increase in the peel, pulp, cut-back juice, and evaporator juice as the ratio increased from 10.5 to 15.9, but the activity definitely decreased by the time a ratio of 18.8 was reached.

Total pectin decreased with increased maturity in all component parts of the fruit, except in the centrifuged juice. The sodium hydroxide-soluble fraction, protopectin, also decreased with increased ratio, while the trend of the polyphosphate-soluble fraction was to increase and that of the water-soluble fraction to decrease. Water-soluble pectin in centrifuged juice remained constant as the Brix/acid ratio increased from 10.5 to 18.8.

Changes in pectinesterase and pectic substances in 42° Brix concentrates were influenced more by processing and short-term storage at elevated temperature than by changes in maturity. Water-soluble pectin, as well as pectinesterase activity, decreased during processing and short-term storage at 80° F., whereas polyphosphate-soluble pectin in-

Table 6

Sum of water and polyphosphate-soluble pectins and clarification and gelation in 42°Brix Pineapple orange concentrates

Maturity Brix/acid ratio	Pectin as anhydrogalacturonic acid per 100 grams of concentrate: Initial g.	After 24 hr. at 80°F. g.	Degree of clarification[d]: Initial from -8°F.	After 24 hr. at 80°F.	Degree of gelation[e]: Initial from -8°F.	After 24 hr. at 80°F.
10.5	0.27	0.28	49-None	98-Extreme	1-Very slight	3-Semi-gel
12.0	0.28	0.29	51-None	97-Extreme	1-Very slight	3-Semi-gel
13.7	0.24	0.23	51-None	97-Extreme	1-Very slight	3-Semi-gel
15.9	0.26	0.27	53-None	95-Extreme	1-Very slight	3-Semi-gel
18.8	0.29	0.29	56-None	96-Extreme	1-Very slight	3-Semi-gel

d Clarification measured by percentage light transmission of centrifuged reconstituted juice using 10 mm. rectangular cell in Lumetron colorimeter with filter No. 730. Degree of clarification: 0 - 59% = none; 60 - 69% = slight; 70 - 84% = definite; 85 - 100% = extreme.

e Gelation: 0 = none; 1 = very slight; 2 = slight; 3 = semi-gel; 4 = solid gel.

creased and sodium hydroxide-soluble pectin remained constant during processing and storage.

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A CITRUS PLANT ELIMINATES WASTE

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The control or treatment of citrus waste has occupied the time and attention of a number of people in recent years. Many have made valuable contributions to the industry but there is still much remaining to be done. It appears that a majority of the attention has been directed towards the treatment of waste. This paper will not discuss the merits of the various approaches to treatment but instead presents a plan to avoid the creation of a waste problem which has been accomplished at the Dunedin Plant of Clinton Foods Inc.

This plant is situated near one of the better residential areas of Dunedin and is within two blocks of Clearwater Bay—a sizable body of salt water. As is too often the case little or no planning was given to the proper treatment of plant waste when the plant was built in 1941. The accepted method of disposing of citrus plant waste was to take the peel and dump it in some suitably distant swamp or to wash it into some convenient stream. The citrus pulp and molasses business was just a dream or beginning to be a reality and was totally untested. Therefore, we had no feed mill or molasses evaporators and all plant wastes with the exception of what peel could be handily collected were pumped into a pond close to the plant, which discharged directly into the bay. It was not long before the residents of this area began to complain bitterly about the odors and debris collecting along the shore line. The small creek which emptied this pond near the plant was filled to a depth of five to six feet with rotting peel and pulp. The odor in that area was extremely unpleasant and the situation rapidly became untenable. In fact the problem became so serious that the local courts ruled to close the plant because it was becoming a public health hazard.

The emergency of the situation forced a decision to install facilities for the manufacture of citrus feed and molasses. This was done at a time when the economy of citrus feed manufacture was doubtful. If, however, the operation broke even, it was a very excellent way of eliminating the waste from the plant and also any court trouble. In addition to the feed mill, Mr. Bristow, our research director, developed a very effective method for treating waste waters which could not be economically converted into molasses.

This treatment consisted of passing waste liquors containing sugars over a screen to remove the solids and through a series of aeration tanks. Six tanks each with a capacity of 25,000 gallons afforded approximately a 60 hour lag. With sufficient air being supplied to the bottom of each tank, a satisfactory fermentation or conversion of sugars to nitrogenous material was accomplished. The effluent from the tank was pumped to the bay where fish and shell life fed on the uncontrolled yeast production.