06-6; (*E*)-**1d**, 83602-15-7; **2a**, 22373-75-7; (*Z*)-**2b**, 487-67-2; (*Z*)-**2c**, 83541-04-2; (*Z*)-**2d**, 3894-82-4; **3a**, 22373-76-8; (*Z*)-**3b**, 22373-74-6; (*E*)-**3b**, 83572-03-6; (*Z*)-**3c**, 83541-05-3; (*E*)-**3c**, 83541-06-4; (*Z*)-**3d**, 83541-07-5; (*E*)-**3d**, 83541-08-6; (4*R*)-**4a**, 83478-03-9; (4*S*)-**4a**, 83541-09-7; **4b**, 83478-04-0; **5a**, 83486-42-4; **5b**, 83478-05-1; **6**, 83478-06-2; **7**, 83478-07-3; **8**, 83478-08-4; **9**, 83478-09-5; **10**, 83478-10-8; **11**, 83478-11-9; **12**, 83478-12-0; **13a**, 83478-13-1; **13b**, 83478-14-2; **13c**, 83478-15-3; **13d**, 83478-16-4; **14a**, 83478-17-5; **14b**, 83478-18-6; **14c**, 83478-19-7; **14d**, 83478-20-0; **15**, 83478-21-1; allyltriphenylphosphonium bromide, 1560-54-9; propyltriphenylphosphonium iodide, 14350-50-6; ethyltriphenylphosphonium iodide, 4736-60-1; (1*R*)-*trans*-chrysanthemoyl chloride, 4489-14-9; [^{13}C]methyltriphenylphosphonium iodide, 81826-67-7; [^{14}C]methyltriphenylphosphonium iodide, 1560-52-7.

Supplementary Material Available: IR and ^{1}H NMR data and ^{13}C NMR data supplemental to those in the text and in Table I (8 pages). Ordering information is given on any current masthead page.

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An Analysis of the Limonin and Naringin Content of Grapefruit Juice Samples Collected from Florida State Test Houses

Richard L. Mansell,* Cecilia A. McIntosh, and Susan E. Vest

An analysis of the limonin and naringin content of 6685 grapefruit juice samples (representing approximately 6% of all grapefruit harvested) collected from three Florida State Test Houses showed that there were statistically significant differences between the Test Houses. There also was a statistically significant difference in the concentration of these compounds in the juice from the different cultivars of fruit sampled. Average limonin and naringin concentrations in the juice remained fairly constant through the beginning of the season until a freeze occurred in early 1981. Juice obtained from fruit harvested after this freeze contained decreasing amounts of limonin and increasing amounts of naringin through the remainder of the season. Results showed that there was no strong correlative relationship between limonin, naringin, Brix, percent acid, and Brix/acid ratio.

The bitterness in grapefruit and processed grapefruit products is primarily due to the presence of two compounds, limonin and naringin. Limonin is an intensely bitter triterpenoid dilactone derivative and is responsible for the "delayed bitterness" in processed citrus products. Naringin is the major flavonoid bitter compound occurring mainly in grapefruit and imparts an immediate bitterness to juice (Maier et al., 1977). Other important qualitative characteristics which affect the organoleptic properties include Brix, acid, and solid content in juice and processed products.

For a number of years accurate and simple tests have been employed for these other qualitative parameters. However, it has been only recently that the routine measurement of limonin and naringin became possible through the development of an accurate, simple, and specific radioimmunoassay (RIA) for limonin (Weiler and Mansell, 1980; Mansell and Weiler, 1980) and a RIA for flavonoid neohesperidosides (primarily naringin) (Jourdan et al., 1982a,b). These two tests have widened the scope of studies in citrus quality research and are presently being adapted for use as routine quality control assays in nonresearch applications. In this paper we present the results of analyses of the limonin and naringin content of juice from individual truckloads of grapefruit from three State Test Houses which were harvested from Oct 1980 through May 1981. The purpose of the present study was to determine whether the content of these two bitter principles was correlated with any of the other qualitative parameters which were being routinely assayed. In addition, we wanted to establish whether there was any relationship between bitter principle concentration and seasonality changes.

MATERIALS AND METHODS

Samples of grapefruit juice were obtained from State Test Houses located at three different processing plants in west-central Florida from Oct 1980 through May 1981. The juice was collected from the same batches used for the determination of Brix and acid and were collected by State Test House personnel. Samples were stored in 1.5-mL plastic vials which contained sodium azide to retard microbial growth, and each vial was labeled with the load number (representing a random sample from approxi-

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Table I. All Juice Samples (n = 6685)

	mean	SD	min	max
lb of juice/box	38.33	2.82	7.81	48.96
% acid	1.31	1.25	0.50	2.21
°Brix	10.67	1.02	1.15	20.85
°Brix/acid ratio	8.35	1.15	1.02	21.20
ppm of limonin	7.52	3.54	0.79	35.97
ppm of naringin	412	148.78	6	2115

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.00	−0.041	−0.059	0.086	0.551	0.006	0.352
lb of juice		1.000	−0.008	0.008	−0.053	−0.096	−0.045
% acid			1.000	0.083	−0.216	−0.046	−0.011
°Brix				1.000	−0.007	−0.173	0.078
°Brix/acid ratio					1.000	0.173	0.221
limonin						1.000	0.106
naringin							1.000

Table II. Test House 1 (n = 1616)

	mean	SD	min	max
lb of juice/box	38.32	3.07	27.01	48.23
% acid	1.27	0.18	0.70	1.93
°Brix	10.72	1.14	1.32	14.72
°Brix/acid ratio	8.58	1.08	1.13	13.70
ppm of limonin	8.19	3.67	1.48	23.37
ppm of naringin	432	152.80	55	2115

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	−0.135	−0.121	0.233	0.366	−0.087	0.255
lb of juice		1.000	0.003	−0.017	−0.019	−0.081	−0.102
% acid			1.000	0.607[a]	−0.696[a]	−0.232	−0.029
°Brix				1.000	0.126	−0.172	0.113
°Brix/acid ratio					1.000	0.140	0.146
ppm of limonin						1.000	0.096
ppm of naringin							1.000

[a] Significance level = 0.0001.

mately 500 boxes of fruit) and the date. The juice was centrifuged 2500g for 5 min to sediment particulate matter, and the supernatant was diluted with water: 500-fold for limonin determinations and 5000-fold for naringin determinations. Aliquots of 0.1 mL were assayed (without further purification) in duplicate by using the ^{3}H-labeled RIA method (Weiler and Mansell, 1980; Jourdan et al., 1982a), and an average value was calculated on a ppm basis. Corresponding data of pounds juice per box, percent acid, Brix, and Brix/acid ratio for each load was provided from the Test House records at the Florida Department of Agriculture office in Winter Haven.

Statistical analyses were performed on an IBM-370 main-frame computer located at the University of South Florida. Statistical programs were taken from a compatible Statistical Analysis System (SAS) pack (SAS Institute, 1979) and standard critical value numbers were obtained from Zar (1974).

RESULTS AND DISCUSSION

In the initial analysis, values from the samples of all Test Houses were combined and the mean, standard deviation, and range of all parameters determined (Table I). The average content of limonin in these 6685 samples was 7.53 ppm with concentrations ranging from 0.79 to 35.95 ppm. An average naringin concentration of 412 ppm was determined and the range of concentration was from 6 to 2115 ppm. Results for pounds juice per box, percent acid, Brix, and Brix/acid ratio are also presented. A Pearson correlation matrix was calculated on this data and no strong correlative relationships between any of the parameters were observed. A study of juice from the 1979–1980 harvest season also revealed the lack of strong correlative relationships between limonin concentration (naringin was not studied), percent acid, Brix, Brix/acid ratio, and pounds juice per box (Mansell and McIntosh, 1980). A study conducted by Kesterson and Hendrix in 1953 showed no correlation between naringin and percent acid, Brix, and Brix/acid ratio; limonin was not determined.

An analysis of the data from each Test House was performed and results are presented in Tables II–IV. Testhouse 1 had the highest mean ppm for both limonin and naringin. Juice samples from Test House 2 had the lowest mean naringin concentration, and the lowest average limonin concentration was observed in the samples from Test House 3. Some differences were observed in the other qualitative parameters, and while all the Test Houses gave the same average pounds juice per box values, the ranges of these values differed. Pearson correlation matrices were calculated for each Test House and the only strong correlations observed were those between percent acid and Brix and Brix/acid ratio in Test Houses 1 and 3 and between date processed and Brix/acid ratio for Test Houses 2 and 3.

For determination of whether observed differences between the State Test Houses were due to the variety of fruit being processed, each cultivar was analyzed separately (Tables V–VII). Juice samples from Duncan grapefruits contained the lowest mean concentrations of both limonin and naringin (6.80 and 375 ppm, respectively). Pink seedless samples contained the highest average limonin

Table III. Test House 2 (n = 3132)

	mean	SD	min	max
lb of juice/box	38.34	2.60	7.81	48.96
% acid	1.35	0.52	0.50	2.11
°Brix	10.52	0.92	1.15	20.85
°Brix/acid ratio	8.16	1.20	1.34	19.06
ppm of limonin	7.45	3.48	0.79	35.97
ppm of naringin	392	145.50	14	1530

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	−0.090	−0.043	−0.012	0.620[a]	0.179	0.340
lb of juice		1.000	−0.004	0.080	−0.172	−0.130	−0.046
% acid			1.000	0.050	−0.219	−0.047	−0.001
°Brix				1.000	−0.098	−0.175	0.033
°Brix/acid ratio					1.000	0.285	0.227
ppm of limonin						1.000	0.164
ppm of naringin							1.000

[a] Significance level = 0.0001.

Table IV. Test House 3 (n = 1937)

	mean	SD	min	max
lb of juice/box	38.33	2.92	26.31	46.58
% acid	1.30	0.20	0.50	2.21
°Brix	10.85	1.03	1.29	14.81
°Brix/acid ratio	8.46	1.07	1.02	21.20
ppm of limonin	7.06	3.45	1.29	24.72
ppm of naringin	428	146.46	6	1800

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	0.089	−0.447	−0.017	0.546[a]	−0.163	0.393
lb of juice		1.000	−0.104	−0.059	0.105	−0.063	0.007
% acid			1.000	0.649[a]	−0.769[a]	−0.094	−0.142
°Brix				1.000	−0.051	−0.171	0.059
°Brix/acid ratio					1.000	−0.012	0.220
ppm of limonin						1.000	0.014
ppm of naringin							1.000

[a] Significance level = 0.0001.

Table V. Duncan Seedy (n = 2870)

	mean	SD	min	max
lb of juice/box	38.35	2.32	7.81	47.16
% acid	1.41	0.17	0.76	2.11
°Brix	10.87	0.90	1.15	20.85
°Brix/acid ratio	7.77	0.82	5.30	13.63
ppm of liminon	6.80	3.19	1.26	35.97
ppm of naringin	375	144.92	14	1800

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	−0.037	−0.284	0.228	0.535[a]	0.081	0.317
lb of juice		1.000	0.017	0.055	−0.085	−0.060	−0.042
% acid			1.000	0.571[a]	−0.741[a]	−0.122	−0.079
°Brix				1.000	0.110	−0.044	0.117
°Brix/acid ratio					1.000	0.116	0.202
ppm of limonin						1.000	0.080
ppm of naringin							1.000

[a] Significance level = 0.0001.

concentration (9.00 ppm), and Marsh seedless had the highest mean naringin concentration (451 ppm). While all cultivars yielded the same average pounds juice per box, pink seedless had the lowest average percent acid and degree Brix and Duncan gave the lowest average Brix/acid ratio. Pearson correlation coefficients were determined, and both Duncan and pink seedless showed a correlative relationship between date processed and Brix/acid ratio and between the percent acid and the Brix and Brix/acid ratio. No strong correlative relationships were observed for Marsh seedless. In a study of 1979–1980 grapefruit juice samples, Mansell and McIntosh (1980) found no strong seasonal correlation was observed between the concentration of limonin in the juice and the date processed. This also was observed in the present study. For example, Marsh grapefruit samples from Test House 1 contained from 4.23 to 18.53 ppm of limonin in Nov 1980 and from 2.88 to 17.48 ppm in March 1981. Similar results were observed for naringin content where Marsh grapefruit juice samples contained between 67 and 644 ppm of nar-

Table VI. Marsh Seedless (n = 2722)

	mean	SD	min	max
lb of juice/box	38.31	3.06	18.83	48.23
% acid	1.28	0.81	0.50	2.21
°Brix	10.59	1.11	1.29	15.04
°Brix/acid ratio	8.63	1.05	1.02	21.20
ppm of limonin	7.68	3.56	0.79	26.26
ppm of naringin	451	140.02	6	1712

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	−0.020	−0.017	0.104	0.371	−0.262	0.210
lb of juice		1.000	−0.025	−0.035	0.009	−0.095	−0.004
% acid			1.000	0.042	−0.221	−0.027	0.012
°Brix				1.000	0.057	−0.207	0.079
°Brix/acid ratio					1.000	0.022	0.089
ppm of limonin						1.000	0.055
ppm of naringin							1.000

Table VII. Pink Seedless (n = 1093)

	mean	SD	min	max
lb of juice/box	38.31	3.31	27.01	48.96
% acid	1.15	0.18	0.70	1.90
°Brix	10.34	0.96	1.32	13.91
°Brix/acid ratio	9.16	1.36	1.15	15.59
ppm of limonin	9.00	3.84	1.29	24.40
ppm of naringin	412	155.13	35	2115

Correlation Coefficients

	date	juice	% acid	°Brix	°Brix/acid	ppm of limonin	ppm of naringin
date	1.000	−0.098	−0.451	0.238	0.628[a]	0.049	0.349
lb of juice		1.000	0.130	0.035	−0.140	−0.159	−0.137
% acid			1.000	0.435[a]	−0.812[a]	−0.251	−0.123
°Brix				1.000	0.147	−0.148	0.190
°Brix/acid ratio					1.000	0.177	0.251
ppm of limonin						1.000	0.153
ppm of naringin							1.000

[a] Significance level = 0.0001.

ingin in Nov 1980 and 157 and 773 ppm of naringin in March 1981.

However, when the data was plotted as the average daily concentration of limonin (or naringin) in the grapefruit juice from each of the three varieties as a function of time (days into the season), a distinct pattern was observed (Figures 1 and 2). On Jan 12, 1981 (corresponding to day 91 on the figures) Florida experienced subfreezing conditions (approximately −7 °C) and this date is noted on the figures. The average daily concentration of limonin in the juice from Marsh grapefruits was fairly steady (albeit variable) for the first 90 days and showed an initial increase after the freeze and a dramatic (and relatively less variable) decrease through the rest of the season (Figure 1). Duncan and pink grapefruit showed similar trends (Figure 1). The average daily concentration of narginin in the juice from Marsh grapefruit showed a trend of increasing naringin through the season (Figure 2), and as with the limonin concentration, points are not as variable after the freeze date. Similar trends were shown by the Duncan and pink grapefruit juice samples (Figure 2). This agrees with earlier observations (Albach et al., 1981; Attaway, 1977) where limonin was seen to decrease over time and naringin concentration increased over time. Therefore, while no strong correlation of bitter principle concentration of individual fruit loads with date was evident, it is apparent that an overall survey of the population of citrus shows the trends described earlier. Table VIII shows the averages of the three varieties for each Test House as well as the overall values of all parameters measured. At this time, with information from only one season with a known freeze date available, it is not possible to determine the effect of freeze on the bitter principle content of juice independent of any seasonal effects.

A general linear model analysis of variance (GLM ANOVA) (SAS Institute, 1979) was performed to test the hypothesis that the average limonin content of the juice from Test House 1 was equal to that of Test House 2 and Test House 3 against the alternate hypothesis that there was an inequality somewhere (α = 0.05). Differences due to cultivars were partitioned out of the error term in order to test only differences due to Test Houses. Where inequalities were detected, significant differences were located by the Student–Neuman–Keuls (SNK) method (Zar, 1974). Similar analyses were performed for pounds juice per box, percent acid, degree Brix, Brix/acid ratio, and ppm of naringin and results are summarized in Table IX. All Test Houses gave the same average yield of juice (pounds juice per box) and the juice from all Test Houses contained equivalent percent acid. The three Test Houses were all significantly different from each other in the Brix/acid ratio, and limonin content of juiced samples. Only Test House 2 was significantly different from the others in naringin concentration. These differences were not due to processing since state regulations guarantee the uniformity of the processing equipment. Another possible explanation for these differences could be the geographical location from which these truckloads of fruit were taken.

It is also possible that these differences could be due to differing environmental or nutritional conditions. In the course of this study a few truckloads of grapefruit yielded juice with high limonin concentration (e.g., 27 ppm). When

Table VIII

variable	Test House 1 D	M	P	over-all	Test House 2 D	M	P	over-all	Test House 3 D	M	P	over-all	all data
lb of juice/box	37.98	38.13	39.00	38.32	38.56	38.26	37.86	38.33	38.19	38.47	37.68	38.33	38.33
% acid	1.31	1.28	1.18	1.27	1.45	1.32	1.13	1.35	1.41	1.24	1.15	1.30	1.31
°Brix	10.97	10.72	10.42	10.72	10.76	10.31	10.27	10.52	11.01	10.77	10.48	10.85	10.67
°Brix/acid ratio	8.42	8.44	8.98	8.58	7.49	8.55	9.28	8.16	7.89	8.82	9.26	8.46	8.35
ppm of limonin	7.51	8.13	9.13	8.19	6.35	8.35	8.88	7.45	7.23	6.81	9.11	7.06	7.52
ppm of naringin	438	437	417	431	355	443	405	392	373	467	439	427	412
n	545	628	443	1616	1554	998	580	3132	771	1096	70	1937	6685
Coefficients of Correlation with Limonin													
ppm of limonin	1.000	1.000	1.000		1.000	1.000	1.000		1.000	1.000	1.000		
ppm of naringin	0.106	0.005	0.198		0.068	0.169	0.109		−0.018	0.063	0.117		
lb of juice/box	−0.096	−0.030	−0.165		−0.044	−0.100	−0.199		0.018	−0.111	0.038		
% acid	−0.046	−0.210	−0.262		−0.057	−0.036	−0.237		−0.114	−0.092	−0.378		
°Brix	−0.173	−0.162	−0.177		−0.030	−0.184	−0.082		−0.101	−0.201	−0.387		
°Brix/acid ratio	0.173	0.101	0.142		0.045	0.136	0.215		0.063	0.055	0.171		
Coefficients of Correlation with Naringin													
ppm of naringin	1.000	1.000	1.000		1.000	1.000	1.000		1.000	1.000	1.000		
ppm of limonin	0.106	0.005	0.198		0.068	0.129	0.109		−0.018	0.063	0.117		
lb of juice/box	−0.045	−0.100	−0.146		−0.009	−0.117	−0.153		−0.046	0.023	−0.043		
% acid	−0.011	−0.003	−0.136		−0.014	−0.023	−0.120		−0.028	0.005	−0.154		
°Brix	0.078	0.098	0.142		0.082	0.056	0.275		0.167	0.064	0.041		
°Brix/acid ratio	0.221	0.105	0.266		0.098	0.094	0.258		0.212	0.043	0.181		

Table IX. Summary of ANOVA[a] and SNK[b] Tests[c]

X	ANOVA conclusions	SNK results[d]
lb of juice/box	accept H_0	
% acid	accept H_0	
°Brix	accept H_1	$2 \neq 1 \neq 3$
°Brix/acid ratio	accept H_1	$2 \neq 3 \neq 1$
ppm of limonin	accept H_1	$3 \neq 2 \neq 1$
ppm of naringin	accept H_1	$2 \neq 3 = 1$

[a] General linear model analysis of variance (SAS Institute, 1979) with differences due to cultivar partitioned out of the error term ($\alpha = 0.05$). [b] Student-Neuman-Keuls test for the location of statistically significant differences (Zar, 1974). [c] H_0: all Test Houses gave juice with the same *X*. H_1: there is an inequality somewhere. [d] Where appropriate, Test Houses are ranked in order of ascending mean parameter (*X*) values.

Table X. Summary of ANOVA[a] and SNK[b] Results[c]

X	ANOVA conclusions	SNK results[d]
lb of juice/box	accept H_0	
% acid	accept H_1	Pink ≠ Marsh ≠ Duncan
°Brix	accept H_1	Pink ≠ Marsh ≠ Duncan
°Brix/acid ratio	accept H_1	Duncan ≠ Marsh ≠ Pink
ppm of limonin	accept H_1	Duncan ≠ Marsh ≠ Pink
ppm of naringin	accept H_1	Duncan ≠ Pink ≠ Marsh

[a] General linear model analysis of variance (SAS Institute, 1979) with differences due to Test Houses partitioned out of the error term ($\alpha = 0.05$). [b] Student-Neuman-Keuls test for the location of statistically significant differences (Zar, 1974). [c] H_0: all cultivars gave juice with the same *X*. H_1: there is an inequality somewhere. [d] Where appropriate, cultivars are ranked in order of ascending mean parameter (*X*) values.

these grapefruit were traced, they were found to have come from an old grove which had been turned into a housing development. These trees had not been fertilized and were obviously under nutritional stress. In the study done on samples from the 1979–1980 season (Mansell and McIntosh, 1980) data analysis showed statistically significant differences between Test Houses for all parameters measured.

The grapefruit cultivars were also compared by using a GLM ANOVA ($\alpha = 0.05$) partitioning differences due to Test House out of the error term in order to test only the differences due to cultivar. The hypothesis tested was that all cultivars gave juice with the same ppm of limonin vs. the alternate hypothesis that there was an inequality somewhere. Where inequalities were detected, significant differences were located by the SNK method. Similar analyses were performed for pounds juice per box, percent acid, degree Brix, Brix/acid ratio, and ppm of naringin, and results are summarized in Table X. There was no statistically significant differences detected in the comparison of the pounds juice obtained per box of fruit. However, in all other analyses, all cultivars were significantly different from each other. Duncan was highest in both percent acid and Brix while pink was the lowest in both of these parameters and Marsh was intermediate. Pink grapefruit gave juice with the highest Brix/acid ratio and the greatest concentration of limonin, Duncan gave the lowest, and again Marsh was intermediate. In the comparison of the naringin concentration, however, Marsh was the highest followed by pink and Duncan was the lowest. In the previous season's study, all cultivars were different from each other for all parameters except for Marsh and Pink for ppm of limonin and percent acid.

In this study we have analyzed completely randomized grapefruit samples for six different qualitative parameters. The results of the limonin and naringin analyses have shown that there is no correlation between the concentrations of these bitter principles and any of the other parameters measured. This lack of correlation was also observed in our 1979–1980 study, thus suggesting that the kinetics of bitter principle production, accumulation, and decline are independent of the other factors which also are involved in grapefruit quality. In addition, in this most recent study the correlative evidence shows that the concentrations of limonin and naringin are independent of each other.

It was also found that each of the cultivars was quite variable and different from the other two in the 1980–1981 season. These differences were also observed in the 1979–1980 season; however, the degree of variability, as reflected in the range of values, was not as great as in the 1980–1981 season. It is important, however, to note that in both years Duncan grapefruit gave juice with the lowest mean limonin concentrations. In 1979–1980, Duncan had

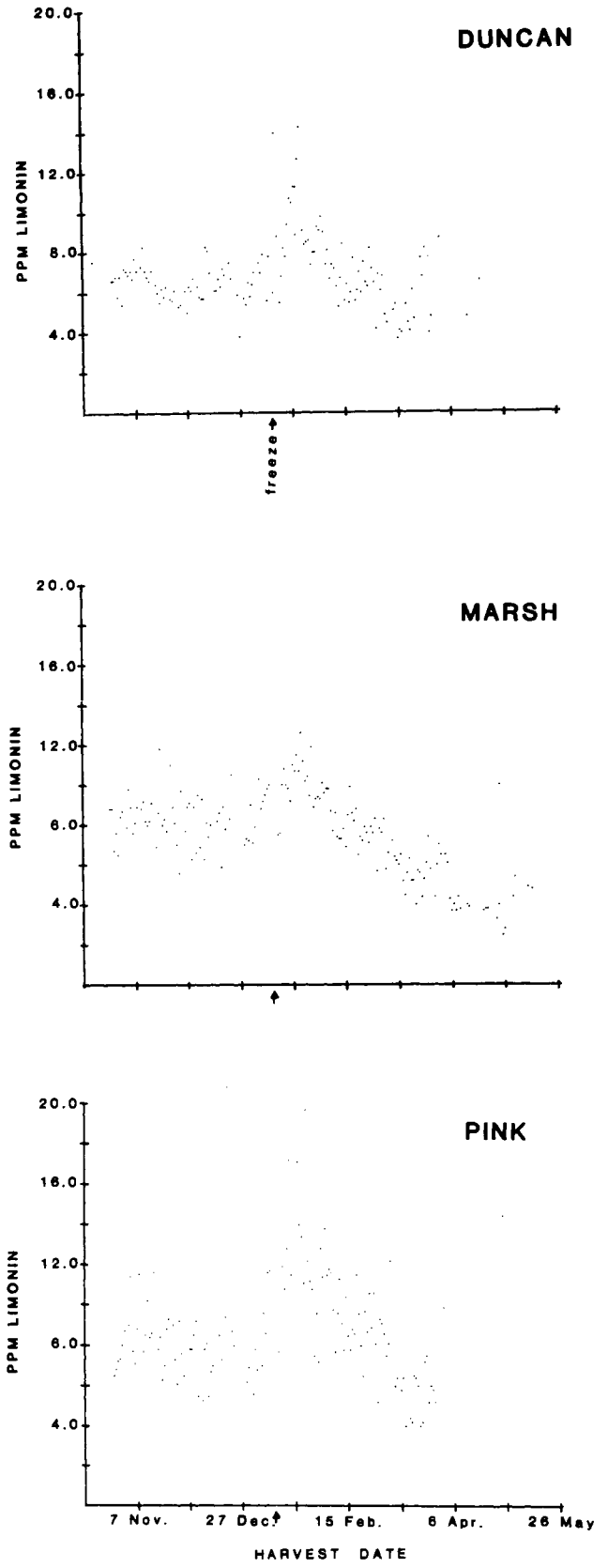

Figure 1. Average daily concentration of limonin in juice samples.

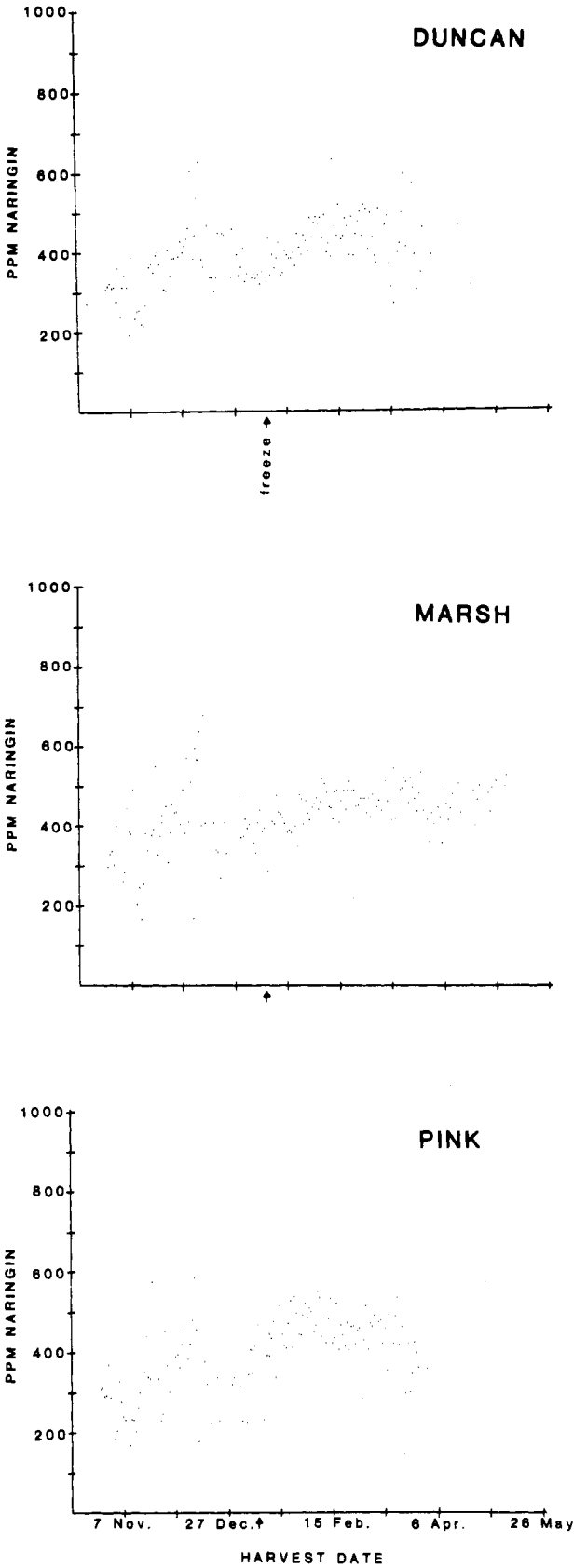

Figure 2. Average daily concentration of naringin in juice samples.

the lowest mean acid and Brix values and Pink the highest whereas in 1980–1981 Pink gave the lowest average acid and Brix values and Duncan the highest. In both seasons Marsh juice samples had intermediate mean values for these parameters.

Individual Test Houses were variable and different from each other in the 1980–1981 season as had been observed in the 1979–1980 season. However, since the same Test Houses were not used for the 1980–1981 season, individual comparisons cannot be made.

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Registry No. Limonin, 1180-71-8; naringin, 10236-47-2.

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COMMUNICATIONS

Solubility Studies of Palm Oil in Practical Extraction Solvents

Simple solubility studies for palm oil in common extraction solvents have been made. Solvents used were *n*-hexane and petroleum ether (bp 60–80 °C). Palm oil was miscible in both solvents at concentrations between 5 and 95% mass fraction. The observed maximum miscibility temperature was 45 °C for oil in *n*-hexane and 48.5 °C in petroleum ether. These solvents would, therefore, be expected to be suitable for the primary extraction of palm oil from the fruit.

Palm oil is the fruit coat fat of the oil palm (*Elaeis guineensis*). It has been an export commodity from, and the preferred domestic vegetable oil in, the southern parts of Nigeria for many years.

In spite of this, relatively little change in extraction technology has occurred over these years even though large plantations and new and higher yielding palms are under cultivation and worldwide demand for palm oil is on the rise. With the possible exception of current developments in Malaysia (Berger, 1978) in which some local processing is being attempted, most extraction technology has been geared to the supply of crude palm oil to the industrial markets in Europe and America where the oil is further treated for industrial purposes or refined to a bland, odorless, nonsmoking, and unidentifiable vegetable oil for home consumption.

Most primary extraction processes consist of cooking and pulping the fleshy portions of the fruit, the product of which is then expressed mechanically or blown with live steam to obtain the crude oil.

During refining, the crude oil is subjected to various treatments—degumming, neutralization, deodorization, bleaching, etc.—with the result that carotene, the only source of vitamin (provitamin A), in the oil is also removed, a situation of some significance in the already vitamin deficient diets in developing countries.

Solvent leaching is a well established vegetable oil extraction technique (Treybal, 1980). Yet not much published data seem to be available on the solubility of palm oil, in fact most vegetable oils, in common extraction solvents. Most published data seem to be concerned mainly with the characterization of these oils (Dean, 1973; Perry, 1963), in terms of their composition, free fatty acid content, saponification number, etc.

We were interested in solvent leaching of palm oil from the fruit in a primary extraction step. Reported here, therefore, are preliminary efforts to determine simple solubility phenomena of local market grade edible palm oil in practical extraction solvents as possible pointers to what may be expected from direct extraction of the oil from the fruit.

EXPERIMENTAL SECTION

Characterization of the Oil. Well-known parameters for characterizing vegetable oils were determined at 29 °C, by using standard methods, for fresh palm oil bought from a local market in Enugu, Nigeria. These parameters were specific gravity, refractive index, acid value, and free fatty acid, by the titration method (Lever Brothers of Nigeria, Ltd., 1978), saponification value, also by the titration method, iodine value, by Wij's method, and peroxide value, by the Lea method (Pearson, 1976). Unsaponifiable matter was determined (Codd et al., 1973) by saponification of the oil with alcoholic KOH, separation of soap in water, extraction of the unsaponifiable matter with ether, and evaporation to dryness.

Reagent-grade *n*-hexane and petroleum ether (bp 60–80 °C) (BD Chemicals, Poole, England) were employed as solvents.

Estimates of Hilderbrandt's solubility parameters, δ (Snyder, 1979), for *n*-hexane and palm oil constituents, for which data could be found, were made to determine that the solvent used would not result in significant preferential solubility of some of the oil constituents. The data are shown in Table I.

It should be noted, however, that Hilderbrandt's parameter δ is not the best index of solubility (Snyder, 1978), especially if, in addition to dispersive forces, dipoles and

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