Chemical Changes during the Development and Ripening of the Fruit of *Cucumis melo* (Cv. Makdimon)

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Changes in the aroma volatiles, free amino acids, sugars, principal acids, and soluble minerals were studied during the development and ripening of the fruit of *Cucumis melo* L. Reticulatis group cv. Makdimon. Ethyl acetate was the most abundant volatile produced during the final growth stage, but ethanol was the major volatile found in immature fruit. Most of the free amino acids exhibited increases in concentration as the fruit underwent the ripening process. Sucrose, although absent in immature fruit, showed a dramatic increase during ripening to become the major carbohydrate constituent in the ripe fruit. The changes in total soluble solids during ripening showed close correlation with those found for pH, certain amino acids, and the elements sodium and potassium. Sucrose concentration has been shown to be an important fruit quality indicator, so these further correlations suggest that some of these parameters may be significant additional determinants of eating quality.

INTRODUCTION

Melons are an important commercial crop in many countries. Many of the most popular cultivars belong to the *C. melo* L. reticulatis group, known as cantaloupe in the United States and rockmelon in Australia. The marked variation in the eating quality of fruit of this type together with the difficulty in detecting their quality by visual inspection represents a barrier to increasing their consumer acceptability.

A number of studies have investigated the relationship between a range of physical and chemical parameters of melons and their sensory evaluation; the most recent are those of Yamaguchi *et al.* (1977) and Mutton *et al.* (1981). Strong correlations between eating quality and the parameters measured were not obtained. These studies suggested that although sweetness or soluble solids values together with aroma and texture were significant determinants of eating quality, other parameters that were not measured may be making important contributions.

A study of the chemical and physicochemical changes occurring during the growth and ripening of a fruit gives an insight into the underlying physiological and biochemical processes taking place. Melons of the reticulatus group exhibit a vigorous climacteric as part of the ripening process that results in marked changes in the properties of the fruit within a comparatively short time frame. The most characteristic of these, a rapid accumulation of sucrose, only occurs if the fruit remains attached to the plant (Pratt, 1970). Harvest before full maturity results in fruit of low sugar content and poor consumer acceptability. On the other hand, harvest at full maturity gives a product of relatively short shelf-life. Achieving a suitable compromise between these two competing factors would be simplified if suitable objective methods for determining fruit maturity were available.

A number of studies of the changes in physiological and chemical parameters of various *C. melo* cultivars have already been carried out (Miccolis and Saltveit, 1991; Augustin *et al.*, 1988; Chachin and Iwata, 1988; Lester and Dunlap, 1985; Srinivas *et al.*, 1983). This investigation extends these studies in terms of the range of parameters studied, particularly the free amino acids, volatiles, and minerals.

MATERIALS AND METHODS

Plant Source. Seeds of Makdimon were sown in peat-perlite medium in $5.0 \times 5.0 \times 8.0$ cm plastic cell pots in September, 1992, and then transplanted (~4 weeks later) into the hydroponic system. Pistillate flowers at anthesis were tagged daily (McGlasson *et al.*, 1963). Fruits that set on the same day were used as sample material. All data obtained were referred to fruit age as days after anthesis (daa). Collection of data was started at 20 days after anthesis and continued at 3−4 day intervals until abscission occurred. Three samples of each maturity rating were analyzed in duplicate.

Sample Preparation for Total Volatiles Analysis. Every individual intact fruit was cored along the equator of the fruit with a cork borer. After removal of the skin, the resulting plugs (5 g) were weighed into a headspace sample vial (20 mL) that was immediately sealed. Samples were left at room temperature (20 min) before analyzing. The external standard consisted of a solution of ethyl butyrate in water (0.1 mg/mL). This solution (2.0 mL) was pipetted into a headspace vial (20 mL) and analyzed with the melon samples. All quantities of volatiles determined were calculated relative to this standard.

Head Space (HS)-GC Analysis of Volatile Compounds. The HS-GC system consisted of a Hewlett-Packard 5890 gas chromatograph, equipped with a Hewlett-Packard 19395A headspace sampler. Samples were separated on a fused silica SE-30 capillary column (J&W Scientific, 30 m × 0.261 mm, 0.25-μm film thickness). Chromatographic conditions were: FID temperature, 220 °C; injector temperature, 170 °C; and carrier gas (nitrogen) pressure, 10.0 psi. The oven temperature was held at 40 °C for 3.5 min after injection, then programmed to 180 °C at 10 °C/min and then immediately increased to 220 °C at 20 °C/min. Data were acquired with HP 3365 series II ChemStation software (Hewlett-Packard).

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The components were identified by comparison of retention times with those of authentic standards. The following conditions were used for the headspace sampler: carrier gas pressure, 0.9 bar; auxiliary pressure, 1 bar; servo air, 3.3 bar; equilibration time, a minimum of one GC run time (~38 min); bath temperature, 105 °C; valve/loop temperature, 110 °C; pressurize time, 15 s; vent/fill loop time, 20 s; inject time, 15 s.

Sample Preparation for Free Amino Acids, Sugars, and Organic Acids. All the mesocarp tissue from each fruit was homogenized in a blender (2 min). Aliquots of the resulting purée (10 g) were quantitatively washed into a volumetric flask (50 mL) with 75% ethanol and left for 10 min. The mixture was filtered, transferred to a storage bottle, and stored at −20 °C until required. Filtrates were allowed to warm to ambient temperature before sampling was carried out.

Preparation of Amino Acid-tBDMS Derivatives. Aliquots of filtrates (5.0 mL) were deproteinized by addition of ethanol (20 mL) and standing at −10 °C for 20 min. Thereafter, the sample was centrifuged at 3500 rpm for 10 min. The supernatant was then transferred to a round-bottom flask (50 mL) and evaporated to dryness under reduced pressure with a rotary evaporator and a 40 °C water bath. To the residue was added the amount of a standard working solution corresponding to 0.1 mg of cycloleucine internal standard. The mixture was cleaned up according to the procedures reported by MacKenzie and Holme (1984) with minor modifications. To the dry residue were added MTBSTFA (150 μL) and DMF (75 μL; Mackenzie *et al.*, 1987), and the mixture was sonicated (15 min) at room temperature and then heated at 110 °C (60 min). After cooling to room temperature, 1 μL of the solution was injected directly into the gas chromatograph.

GC Analysis of Amino Acid-tBDMS Derivatives. The gas chromatograph and the column used were as already described. The chromatographic conditions were: injection temperature, 240 °C; FID temperature, 290 °C; the oven temperature was programmed from 120 to 170 °C at a rate of 5 °C/min and then to 280 °C at a rate of 4 °C/min and held for 20 min; and injection was by the split mode (ratio 1:30). The rest of the conditions and data acquisition were as already described.

Analysis of Sugars and Organic Acids. The filtrates obtained above (200 μL) were analyzed according to the method of Chapman and Horvat (1989) with minor modifications. Identification of the components was achieved by comparison of their retention times and mass spectra with those of authentic standards.

pH Measurement. Mesocarp tissues from each melon were homogenized in a blender (2 min). The pH of the resulting purée (50 g) was measured with a Beckman Φ50 pH meter.

Total Soluble Solids Determination. The purée (50 g) was centrifuged at 3500 rpm for 10 min. The total soluble solids (expressed as degrees Brix) of the supernatant was measured with an ABBE refractometer maintained at 20 °C and calibrated against pure water.

Soluble Mineral Analysis. The supernatant (1.38 mL) prepared from centrifuging melon purée was diluted with 0.2 M HCl to 10 mL. The resulting solution was analyzed directly with a Labtam Plasmalab Coupled Polychromator/monochromator (Melbourne, Australia), which was configured to measure B, Cu, Zn, Ca, Fe, Mn, Mg, Na, K, P, and S. External calibration standards were run between every 10 samples. The standard solution contained 520 μg/mL Ca (CaCO$_3$) and Na (Na$_2$CO$_3$), 1950 μg/mL K (K$_2$CO$_3$), 420 μg/mL P (NH$_4$H$_2$PO$_4$), and 100 μg/mL Mg (MgCO$_3$). Trace elements at levels of parts per billion (ng/mL) were dissolved and added to the standard solution.

Statistical Analysis. Statistical analyses were performed with the Microsoft Excel package.

RESULTS AND DISCUSSION

The correlation coefficients between the changes in concentrations of the range of parameters measured in the fruit of cv. Makdimon melons during their develop-

ment and ripening are listed in Table 1. There are many significant correlations among these parameters, but two groups of compounds are notable for their close interrelationships. The first group is characterized by a strong correlation (>0.87) between the changes in the total soluble solids (TSS) values with those for flesh pH, total sugars, total volatiles, and the soluble minerals potassium and sodium. If the TSS is regarded, as is often the case, as an indicator of fruit maturity, then clearly each or all of the parameters mentioned may also perform this function. Therefore, these overall parameters are an outward indication of the intense biochemical activity taking place within the fruit during ripening and represent factors that may need to be taken into account as quality determinants during sensory analysis.

The second group of compounds with close interrelationships consists of the majority of the free amino acids in the amino acid pool whose concentration changes were significantly correlated both with TSS and with each other during fruit development and ripening. The only amino acids measured that did not show this behavior were glutamine, citrulline, and lysine whose concentration changes were negatively correlated with those of TSS and the other amino acids. All of the remaining amino acids showed marked increases in their concentrations during the ripening period.

Changes in the concentrations of many of the minerals also correlated closely with those of TSS, with potassium and sodium exhibiting highly significant correlation coefficients. An exception to this was calcium, which showed large and negative correlations with almost all of the changes observed for the other parameters. Copper also showed a similar, though less pronounced, relationship.

Free Amino Acids and Total Volatiles. The biogenetic relationship between the formation of aroma volatiles and the free amino acids present in ripening fruit is well established (Schreier, 1984). In particular, the amino acids valine, isoleucine, methionine, and alanine can be postulated as precursors of the majority of the esters found in melons (Wyllie *et al.*, 1993; Hansen and Poll, 1993). This interrelationship is supported by the data in Table 1, which show that the changes in concentrations of these and some other amino acids are well correlated with the production of the total volatiles. The composition and concentration of the amino acids in the amino acid pool during ripening, together with the activities of the enzyme systems required for their conversion to esters, are therefore the major determinants of the quantity and quality of the resulting aroma profile. The changes in the free amino acids found in the fruit of Makdimon between 20 and 48 daa are shown in Table 2. The majority of the amino acids showed a marked increase in concentration during the ripening phase of development. Indeed, as is shown in Table 1, the changes in concentrations of almost all of the amino acids except those just mentioned showed medium to strong correlations with the changes observed for the total volatiles. A similar correlation between the production of aroma components in bananas and the increase in the amounts of the amino acids valine and leucine was suggested by Tressl and Drawert (1973). However, in this case, the concentrations of the other amino acids monitored, including that of isoleucine, remained constant during the development period. This observation implies that the type and extent of ester formation may be determined by substrate availability in this fruit. In ripe, high quality melons, the total volatiles concentration can reach values of >100 mg/
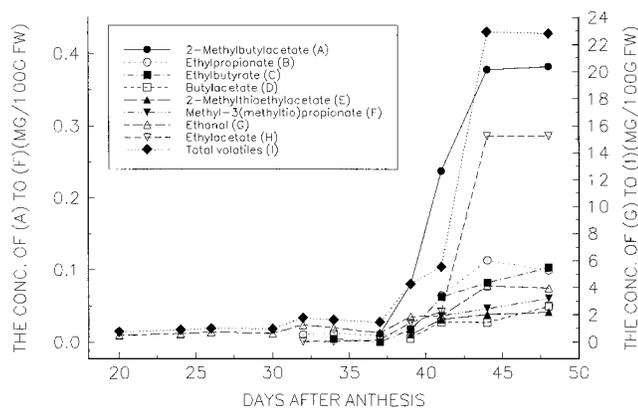
Table 1. Correlation Coefficients between Total Soluble Solid Content, Total Sugar, pH, Some Amino Acids, and Soluble Minerals in Makdimon Melons[a]

variable	TSS	TS	pH	TV	Val	Leu	Ile	Ser	Thr	Pro	Pip	K	Na	inositol	Mg	P	S	Ca	Mn	B	Fe	Zn	Cu	Ala	Gly	GABA	Met	Phe	Asp	Glu	Tyr	Asn	Gln
Ts	0.948																																
pH	0.945	0.875																															
TV	0.873	0.907	0.823																														
Val	0.903	0.892	0.883	0.877																													
Leu	0.843	0.784	0.792	0.738	0.950																												
Ile	0.798	0.711	0.780	0.654	0.915	0.973																											
Ser	0.908	0.926	0.878	0.913	0.980	0.903	0.835																										
Thr	0.916	0.883	0.893	0.826	0.976	0.932	0.904	0.964																									
Pro	0.876	0.869	0.835	0.860	0.961	0.919	0.849	0.965	0.956																								
Pip	0.793	0.836	0.759	0.872	0.904	0.859	0.792	0.921	0.865	0.918																							
K	0.930	0.922	0.872	0.745	0.910	0.860	0.799	0.905	0.931	0.907	0.828																						
Na	0.922	0.851	0.886	0.798	0.918	0.866	0.813	0.908	0.918	0.895	0.886	0.950																					
inositol	0.858	0.888	0.804	0.860	0.833	0.732	0.686	0.835	0.771	0.784	0.619	0.698	0.694																				
Mg	0.683	0.616	0.595	0.533	0.690	0.717	0.669	0.650	0.736	0.730	0.639	0.853	0.744	0.426																			
P	0.759	0.691	0.779	0.545	0.738	0.681	0.636	0.754	0.792	0.748	0.786	0.850	0.757	0.595	0.282																		
S	0.526	0.598	0.618	0.771	0.678	0.463	0.429	0.707	0.566	0.582	0.715	0.567	0.660	0.656	0.656	0.565																	
Ca	-0.876	-0.760	-0.808	-0.593	-0.782	-0.810	-0.749	-0.764	-0.812	-0.787	-0.717	-0.785	-0.819	-0.665	-0.506	-0.585	-0.358																
Mn	0.632	0.648	0.547	0.473	0.557	0.511	0.456	0.613	0.540	0.518	0.539	0.596	0.513	0.514	0.600	0.539	0.283	-0.371															
B	0.595	0.581	0.513	0.701	0.671	0.610	0.533	0.613	0.540	0.681	0.691	0.557	0.623	0.590	0.479	0.259	0.527	-0.505	0.344														
Fe	0.759	0.706	0.551	0.487	0.628	0.655	0.601	0.624	0.667	0.637	0.574	0.715	0.650	0.495	0.654	0.744	0.282	-0.662	0.651	0.431													
Zn	0.548	0.599	0.534	0.526	0.544	0.444	0.350	0.607	0.588	0.653	0.491	0.580	0.485	0.586	0.461	0.555	0.377	-0.526	0.178	0.298	0.331												
Cu	-0.022	0.001	-0.006	0.007	0.013	-0.013	-0.021	0.020	-0.022	-0.070	-0.052	-0.048	0.001	-0.006	0.001	0.090	0.264	0.051	-0.044	0.001	-0.058	-0.012											
Ala	0.673	0.755	0.567	0.829	0.765	0.697	0.575	0.842	0.754	0.801	0.859	0.628	0.671	0.634	0.426	0.445	0.568	-0.493	0.353	0.393	0.464	0.411	-0.003										
Gly	0.708	0.756	0.675	0.780	0.852	0.758	0.726	0.863	0.827	0.888	0.846	0.696	0.722	0.721	0.438	0.521	0.637	-0.616	0.338	0.539	0.378	0.565	-0.004	0.805									
GABA	0.883	0.837	0.878	0.644	0.777	0.758	0.726	0.773	0.799	0.780	0.698	0.826	0.788	0.726	0.607	0.716	0.347	-0.781	0.572	0.410	0.539	0.516	-0.079	0.479	0.608								
Met	0.800	0.738	0.802	0.785	0.776	0.693	0.660	0.757	0.740	0.745	0.639	0.820	0.875	0.745	0.580	0.611	0.630	-0.807	0.397	0.614	0.575	0.533	-0.018	0.533	0.470	0.691							
Phe	0.796	0.780	0.781	0.785	0.825	0.804	0.735	0.838	0.811	0.869	0.844	0.743	0.747	0.731	0.535	0.602	0.358	-0.795	0.389	0.624	0.571	0.533	-0.151	0.663	0.530	0.651	0.799						
Asp	0.800	0.705	0.749	0.509	0.663	0.652	0.584	0.757	0.758	0.726	0.639	0.709	0.709	0.636	0.574	0.533	0.182	-0.848	0.624	0.466	0.780	0.431	-0.154	0.342	0.516	0.431	0.605	0.716					
Glu	0.819	0.812	0.824	0.792	0.803	0.742	0.681	0.816	0.779	0.823	0.794	0.740	0.737	0.773	0.528	0.595	0.442	-0.752	0.443	0.607	0.543	0.568	-0.128	0.581	0.580	0.870	0.502	0.690	0.530				
Tyr	0.739	0.586	0.775	0.490	0.586	0.661	0.701	0.612	0.746	0.663	0.771	0.760	0.541	0.669	0.725	0.446	0.360	-0.725	0.446	0.430	0.572	0.257	-0.115	0.502	0.690	0.664	0.530	0.752	0.492	0.558			
Asn																															0.716		
Gln	-0.495	-0.487	-0.530	-0.565	-0.612	-0.558	-0.522	-0.598	-0.549	-0.572	-0.621	-0.312	-0.425	-0.626	-0.045	-0.240	-0.478	0.499	-0.212	-0.362	-0.116	-0.208	-0.502	-0.557	-0.633	-0.389	-0.539	-0.546	-0.370		-0.523	-0.233	
Om+Cit	-0.464	-0.426	-0.370	-0.394	-0.495	-0.522	-0.463	-0.475	-0.521	-0.546	-0.361	-0.434	-0.416	-0.335	-0.350	-0.268	-0.147	0.482	-0.188	-0.395	-0.348	-0.368	-0.379	-0.329	-0.335	-0.080	-0.240	-0.303	-0.184		-0.486	-0.355	

[a] r crit. (p < 0.001, df = 30) = 0.554; r crit. (p < 0.01, df = 30) = 0.449; r crit. (p < 0.05, df = 30) = 0.349.

Table 2. Free Amino Acid Concentrations (mg/100 g fw) in Makdimon Melons at Different Stages of Maturity[a]

daa	Ala	Thr	Gly	Val	Leu	Ile	Pro	GABA	Met	Pip	Ser
20	0.941 ± 0.358	2.650 ± 0.276	1.499 ± 1.007	2.992 ± 0.285	2.341 ± 0.225	1.972 ± 0.163	1.037 ± 0.103	10.569 ± 1.632	0.458 ± 0.309	0.259 ± 0.014	3.704 ± 0.130
24	1.853 ± 0.058	3.569 ± 0.679	1.283 ± 0.288	3.440 ± 0.334	2.509 ± 0.773	2.546 ± 0.496	1.007 ± 0.108	10.719 ± 0.828	0.376 ± 0.046	0.261 ± 0.066	3.013 ± 1.120
26	2.892 ± 0.233	3.787 ± 0.106	1.894 ± 0.672	3.837 ± 0.650	3.479 ± 0.562	2.606 ± 0.547	1.539 ± 0.293	18.649 ± 1.741	0.226 ± 0.006	0.179 ± 0.053	4.723 ± 0.530
30	2.919 ± 0.467	4.148 ± 0.607	1.386 ± 0.684	3.214 ± 0.415	2.548 ± 0.227	2.094 ± 0.251	2.083 ± 0.318	19.664 ± 3.536	0.454 ± 0.345	0.222 ± 0.062	4.202 ± 0.500
32	5.930 ± 5.338	4.854 ± 1.391	2.022 ± 0.130	4.701 ± 1.530	3.968 ± 0.930	2.869 ± 0.686	2.225 ± 0.229	22.186 ± 8.657	0.990 ± 0.432	0.260 ± 0.020	5.785 ± 2.220
34	3.060 ± 1.516	4.228 ± 0.562	1.206 ± 0.418	3.816 ± 0.620	3.415 ± 0.315	2.584 ± 0.225	1.836 ± 0.307	22.128 ± 3.813	1.005 ± 0.192	0.280 ± 0.031	5.348 ± 0.715
37	2.619 ± 2.812	5.274 ± 0.821	1.809 ± 1.170	5.720 ± 1.390	4.510 ± 0.857	3.413 ± 0.616	2.115 ± 0.345	37.274 ± 13.851	1.430 ± 0.177	0.295 ± 0.048	7.432 ± 1.826
39	1.017 ± 0.513	7.312 ± 0.687	2.112 ± 0.852	8.178 ± 1.002	6.012 ± 0.756	4.625 ± 0.696	3.112 ± 0.407	48.114 ± 17.494	1.647 ± 0.319	0.412 ± 0.088	11.130 ± 1.230
41	2.337 ± 3.058	8.103 ± 1.926	2.924 ± 0.574	9.532 ± 2.092	6.008 ± 0.618	4.543 ± 0.520	3.776 ± 0.707	51.054 ± 11.654	2.613 ± 0.717	0.410 ± 0.002	14.290 ± 4.441
44	21.334 ± 6.581	9.579 ± 0.421	3.777 ± 0.352	11.827 ± 1.359	5.927 ± 0.616	3.942 ± 0.439	4.633 ± 0.089	56.218 ± 3.539	3.480 ± 0.288	0.620 ± 0.098	23.340 ± 1.871
48	23.891 ± 14.85	10.541 ± 2.044	4.840 ± 1.732	15.038 ± 1.885	8.993 ± 1.518	5.830 ± 0.645	6.185 ± 1.269	51.008 ± 13.112	3.646 ± 2.288	0.883 ± 0.264	26.234 ± 6.424

daa	Phe	Asp	Glu	Lys	Tyr	Asn	Gln	Cit
20	1.190 ± 0.458	6.069 ± 0.465	23.699 ± 6.642	1.479 ± 0.000	0.665 ± 0.422	2.742 ± 0.215	166.808 ± 75.685	60.894 ± 41.454
24	1.358 ± 0.591	5.775 ± 0.672	25.790 ± 0.941	1.111 ± 0.318	0.686 ± 0.460	2.695 ± 0.295	188.879 ± 35.006	68.782 ± 18.908
26	0.846 ± 0.212	6.690 ± 0.785	22.866 ± 2.713	1.800 ± 0.243	0.264 ± 0.067	3.120 ± 0.417	272.370 ± 30.787	38.217 ± 8.760
30	1.534 ± 0.867	12.655 ± 2.654	31.522 ± 3.660	1.425 ± 0.000	0.725 ± 0.602	3.922 ± 0.861	273.472 ± 80.652	39.822 ± 29.384
32	2.484 ± 1.056	17.816 ± 3.891	26.217 ± 6.678	1.356 ± 0.344	1.252 ± 0.868	3.938 ± 0.238	201.567 ± 87.489	38.047 ± 8.170
34	2.792 ± 0.564	20.205 ± 2.479	26.051 ± 8.667	1.143 ± 0.081	1.642 ± 0.325	3.571 ± 0.912	191.505 ± 7.731	42.439 ± 8.743
37	2.587 ± 0.663	24.975 ± 3.911	22.165 ± 4.807	1.468 ± 0.493	1.390 ± 0.762	3.830 ± 0.575	172.420 ± 26.566	33.161 ± 19.135
39	2.916 ± 1.215	28.098 ± 3.306	37.156 ± 2.676	1.159 ± 0.301	1.818 ± 1.136	5.533 ± 0.584	205.294 ± 60.870	39.638 ± 25.946
41	4.112 ± 0.537	19.115 ± 4.941	45.079 ± 25.240	1.164 ± 0.041	2.654 ± 0.227	5.112 ± 0.389	151.598 ± 41.346	29.692 ± 11.396
44	4.662 ± 0.363	29.586 ± 7.859	85.983 ± 10.250	0.902 ± 0.000	3.290 ± 0.125	5.110 ± 0.164	140.510 ± 23.890	31.552 ± 9.262
48	6.599 ± 1.911	22.604 ± 4.633	66.207 ± 29.160	1.907 ± 0.000	4.008 ± 1.000	4.466 ± 0.692	76.122 ± 11.117	19.568 ± 9.421

[a] Data are the average of three fruits from one harvest; values are expressed as means ± standard deviation for each measurement.

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Figure 1. Changes in some aroma volatiles of cv. Makdimon melons during ripening.

kg, a figure that requires significant quantities of precursors for their formation. It appears that the ripening fruit increases the supply of amino acids to meet the demand for ester precursors. Of particular note is that, in melons, the concentrations of leucine and isoleucine throughout the ripening phase remain very similar (Table 2), but the aroma esters formed are characterized by having carbon skeletons derived almost exclusively from isoleucine. Thus, at some point in the series of steps bringing about this ester formation, a considerable degree of selectivity, presumably a property of the enzymes involved, must take place as the substrates are drawn from the amino acid pool. This selectivity is likely to be genetically determined and will have a profound influence on the volatile ester profile of the fruit. It may explain the variation found in the composition of esters obtained from different varieties or cultivars of melons (Yamaguchi *et al.*, 1977; Wyllie *et al.*, 1992).

Glutamine is present in young fruit (20 daa) at a high concentration, which continues to increase up to 30 daa after which it decreases steadily. This pattern is generally in agreement with that found for the melon cv. Prince, as reported by Hashinaga *et al.* (1984) and Chachin and Iwata (1988), and with the changes observed in tomato by Liu and Luh (1979). Glutamine is known to be an important nitrogen transport compound in plants (Joy, 1988), so this pattern presumably reflects the changes in the need for this element as growth processes are progressively taken over by the ripening (Chaturvedi *et al.*, 1979; Kluba *et al.*, 1978). Free amino acids may make a contribution to the flavor quality of the fruit in a direct manner, either by their own taste or by their taste-enhancing capacity, as exemplified by L-glutamate, or by their buffer affect (Petró-Turza, 1986–87). The taste threshold concentration of pure amino acids was reported to range from 0.03 (Asp) to 3.0 g/L (Pro), and their tastes vary from sweet (i.e., Ala), to sour (i.e., Asp), to bitter (i.e., Leu and Ile; Kirimura *et al.*, 1969; Hardy, 1985).

Aroma Volatiles. The changes in total volatiles and principal volatiles components of Makdimon melon fruit during development are shown in Figure 1. The only volatile observed in immature fruit was ethanol. Ethyl acetate began to accumulate some 32 days after anthesis and increased markedly with increasing maturity of the fruit, reaching a maximum level of 15.5 mg/100 g (fw) at 43 daa, a value which accounted for 66.8% of total volatiles at this time. Most of the other volatiles measured began to develop about the same time as ethyl acetate or somewhat later, although 2-methylbutyl acetate, another major volatiles constituent, begins a

rapid rise in concentration 2–3 days before ethyl acetate. The concentrations of most of the esters were at a maximum just before the fruit full slip. Similar observations for these compounds have been previously reported by other investigators (Yabumoto *et al.*, 1978; Horvat and Senter, 1987).

TSS, TS, and pH. The detailed composition of the total sugars found in the fruit of Makdimon during development is shown in Table 3. The results are similar to those reported by McCollum *et al.* (1988), Lester and Dunlap (1985), Hashinaga *et al.* (1984), and Chachin and Iwata (1988) for other varieties. Fructose, glucose, and sucrose are the major components. For the first 35 days after anthesis, fructose and glucose predominate. The fructose content varied between 1.3 and 2.0% during the course of fruit development, whereas the glucose content increased in young fruit from ~1.3% to a maximum of ~1.8–1.9%, and then dropped during ripening to 1.2%. The reduction in content of both monosaccharides may make a contribution to the accumulation of sucrose (Lester and Dunlap, 1985). The commencement of ripening at 32 daa is marked by the appearance of sucrose, which dramatically increases in concentration as the process continues. Sucrose reached levels of between 4.3 and 6.9% on a fresh weight basis in fully ripe melons. Therefore, the rapid increase in total sugars during ripening is entirely due to the accumulation of sucrose. The only other carbohydrate detected under the analysis conditions used was inositol. Inositol was found only in low concentrations (0.07–0.13%), with the higher values appearing as the fruit approached maturity. Hashinaga *et al.* (1984) also found inositol in ripe cv. Prince melon.

The pH of the mesocarp increased over the lifetime of the fruit from a value of ~5.3 to a maximum of 6.75 (Table 3). The changes in pH are not correlated with the rather small changes in measured organic acid concentrations that occur throughout the development process. Strong correlations between the changes in pH and the changes in TSS and TS over the lifetime of the fruit were observed (Table 1), indicating that there is a relationship between the rise in pH and the accumulation of sucrose. The enzymatic changes involved in the synthesis and degradation of sucrose in melon fruit have been quite extensively studied (Schaffer *et al.*, 1987; Hubbard *et al.*, 1989; Lingle and Dunlap, 1987). The enzymes soluble acid invertase and sucrose phosphate synthase play important roles in sucrose accumulation. Acid invertase, the enzyme responsible for sucrose cleavage, shows a marked decrease in activity during ripening that retards further sucrose degradation. The increase in sucrose phosphate synthase activity, on the other hand, has been shown to correlate with the increase in sucrose concentration (Hubbard *et al.*, 1989). The factors that bring about the changes in the activities of these enzymes during the development cycle are not known. However, the changes in the pH of the fruit flesh during ripening suggest that changes in enzyme activity could have a role in the switch from sucrose degradation to sucrose accumulation because the enzymes involved have different pH optima (McCollum *et al.*, 1988). The pH will also influence the sensory quality of the fruit because it affects the taste response.

Organic Acids. The only organic acids found in significant concentrations in the fruit of cv. Makdimon were succinic acid and citric acid. Succinic acid appeared in notable concentrations (~0.2%) in the immature fruit (i.e., between 20 and 26 daa) but was not detected thereafter until it was found in the fully mature fruit (40 daa) in low concentrations (Table 3).

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Table 3. pH, Organic Acid, TSS, and Sugar Content of Makdimon Melons at Different Stages of Maturity[a]

days after anthesis	pH	TSS % (w/w)[b]	total sugar % (w/w)	fructose % (w/w)	glucose % (w/w)	sucrose % (w/w)	inositol % (w/w)	succinic acid % (w/w)	citric acid % (w/w)
20	5.52 ± 0.05	4.97 ± 0.20	2.69 ± 0.33	1.34 ± 0.05	1.31 ± 0.28	—[c]	0.08 ± 0.02	0.26 ± 0.01	—
24	5.35 ± 0.01	5.13 ± 0.31	3.12 ± 0.06	1.59 ± 0.05	1.53 ± 0.04	—	0.07 ± 0.00	0.22 ± 0.00	0.07 ± 0.00
26	5.28 ± 0.11	5.53 ± 0.42	3.58 ± 0.29	1.82 ± 0.16	1.76 ± 0.14	—	0.06 ± 0.00	0.11 ± 0.08	0.19 ± 0.04
30	5.31 ± 0.04	6.00 ± 0.10	3.50 ± 0.22	1.76 ± 0.10	1.74 ± 0.12	—	0.07 ± 0.00	—	0.31 ± 0.00
32	5.46 ± 0.05	6.30 ± 0.36	3.68 ± 0.00	1.85 ± 0.03	1.81 ± 0.07	0.07 ± 0.00	0.08 ± 0.00	—	0.32 ± 0.04
34	5.64 ± 0.22	6.67 ± 0.42	3.87 ± 0.44	1.98 ± 0.22	1.85 ± 0.21	0.09 ± 0.01	0.07 ± 0.01	—	0.26 ± 0.03
37	5.80 ± 0.09	7.87 ± 1.01	5.02 ± 1.03	1.94 ± 0.05	1.91 ± 0.04	1.17 ± 1.00	0.09 ± 0.01	—	0.28 ± 0.03
39	6.26 ± 0.21	8.50 ± 0.36	5.11 ± 1.19	1.81 ± 0.19	1.65 ± 0.10	1.65 ± 1.29	0.08 ± 0.00	—	0.24 ± 0.02
41	6.39 ± 0.21	8.77 ± 0.40	5.61 ± 0.72	1.81 ± 0.38	1.49 ± 0.35	2.31 ± 1.41	0.10 ± 0.01	—	0.26 ± 0.07
44	6.78 ± 0.03	11.17 ± 0.15	9.05 ± 1.51	2.03 ± 0.09	1.40 ± 0.15	5.62 ± 1.32	0.12 ± 0.03	—	0.20 ± 0.06
48[d]	6.48 ± 0.08	10.48 ± 0.62	8.35 ± 1.08	1.77 ± 0.30	1.20 ± 0.27	5.38 ± 0.72	0.13 ± 0.02	0.06 ± 0.01	0.12 ± 0.04

[a] Data are the average of three fruits from one harvest and are expressed as mean ± standard deviation. [b] Percent fresh weight of edible portion. [c] —, Undetected. [d] The value for 48 daa is the average of 10 fruits.

Citric acid, on the other hand, was not found in the most immature fruit studied (20 daa), but all later samples showed citric acid concentrations ranging from 0.06 to 0.12% (Table 1). The maximum value was reached at 30−32 daa and then declined steadily over the remainder of the life of the fruit. Hashinaga *et al.* (1984) reported the presence of low concentrations of formic, acetic, butyric, lactic, oxalic, malonic, and malic acids, as well as larger amounts of citric acid in cv. Prince melons, but Chachin and Iwata (1988) mentioned only malic and citric acids as being present in their work on the same cultivar. None of the acids mentioned, except succinic and citric, were found in this investigation, but they may well have been present in concentrations below the limit of detection of the analytical protocol used.

Soluble Minerals. Under normal growing conditions, the minerals found in fruit would reflect the mineral content of the soil and of any applied fertilizers. In this investigation, because the melons were grown hydroponically, the mineral content should reflect the composition of the nutrient solutions used. Because this composition was maintained as constant as possible, the changes, if any, observed in the mineral content would be expected to arise from physiological or biochemical processes associated with growth and development. On the other hand, use of hydroponically grown melons does not provide a basis for comparison with the results obtained by other workers using field grown material.

The concentrations of the minerals measured in developing melon fruit are shown in Table 4. Potassium is a major component of the mineral pool of melon fruit, with a concentration of ∼3400 µg/mL in the juice of ripe fruit. Potassium exhibits a marked increase in concentration during the ripening period that, as mentioned previously, exhibits a strong correlation with changes in both TSS and TS. Potassium has been considered to be associated with the translocation of photosynthates to fruit (Shear, 1980) and is thought to play an important role in ion balance. It may be required to maintain cell organization and permeability (Lui and Luh, 1979). The large increase in the potassium concentration in the fully ripe fruit could have a number of consequences. The presence of salts may influence the perception of sweetness. De Bruyn *et al.* (1971) have shown that for tomatoes, sensory panel members favored samples to which salts (potassium citrate) were added. Potassium also affected the titratable acidity of these fruit and hence the intensity of the sour taste (Koo and Reese, 1977; Stevens, 1972). Moreover, it is known that potassium also influences the activity of some enzymes. The key regulatory steps in glycolysis are catalyzed by the enzymes phosphofructokinase and pyruvate kinase, both of which have been shown to be susceptible to a wide range of modulators (Seymour *et al.*, 1993). Potassium and phosphate act as activators of these enzymes and, hence, the increase in the concentrations of both of these elements during ripening may be contributing to the increased respiration rates associated with this process. The activity of the ester forming enzyme acyl acetyl CoA transferase (AAT) in banana and strawberry fruits has also been shown to be stimulated by the presence of potassium (Harada *et al.*, 1985; Pérez *et al.*, 1993). Thus, the increase in potassium concentration during the ripening may serve to substantially increase the activity of this enzyme and, hence, promote the production of the volatile esters characteristic of the melon aroma profile.

Phosphorus was the second most abundant mineral component in melon fruit. A large increase in concentration that coincided with the onset of ripening was observed. Pratt (1970) suggested that the rapid synthesis of sucrose as melons matured was correlated with high rates of formation of high-energy phosphate. We observed a moderately significant correlation (0.566; $p < 0.05$) between changes in phosphorus and sucrose concentrations. As shown in Table 1, the changes in calcium concentration are negatively correlated with TSS development. The soluble calcium concentration decreased markedly from 20 to 7 mg/100 g (fw) over the growth period. Similar observations were reported by Lester and Dunlap (1985) who found total calcium declined from 1100 to 800 mg/100 g in Perlita muskmelon fruits. Hashinaga *et al.* (1984) found the calcium concentration of immature Prince melons to be 1.08 mg/100 g, falling to 0.7 mg/100 g in ripe and 0.6 mg/100 g in overripe fruit. A fall in the calcium concentration in melons appears to be an essential step in the regulation of ripening and to be related to cell division for textural softening through its effect of stabilizing the pectin matrix of the cell wall (Kermasha *et al.*, 1987). The results obtained by Cutting *et al.* (1992) on avocados showed that fruit with a lower calcium concentration ripened more rapidly, suggesting that calcium concentration exerts a major influence on the rate of fruit ripening. This conclusion may also apply to melon fruit.

The magnesium ion content generally showed an steady increase during growth and ripening. Shear *et al.* (1980) believed that the activity of this element in fruits is related to that of calcium because the maintenance of an adequate supply of magnesium is an important factor in ensuring efficient calcium uptake. A weak negative correlation between the changes in these two elements was observed.

Conclusions. Significant changes occur in the concentrations of many chemical components of melons during the ripening phase of fruit development. Some or some combination of these components may either

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Table 4. Mineral Content (µg/mL in juice) of Makdimon Melons at Different Stages of Maturity[a]

daa	B	Ca	Cu	Fe	K	Mg	Mn	Na	P	S	Zn	Mo
20	0.58 ± 0.17	197.57 ± 18.53	0.56 ± 0.08	0.48 ± 0.03	1824.16 ± 17.41	119.54 ± 9.08	0.35 ± 0.03	28.93 ± 1.45	226.03 ± 25.29	46.04 ± 6.11	0.04 ± 0.07	0.09 ± 0.08
24	0.59 ± 0.17	165.15 ± 11.25	0.97 ± 1.02	1.04 ± 0.08	2049.16 ± 77.61	127.08 ± 5.11	0.32 ± 0.01	38.61 ± 2.90	221.74 ± 16.33	41.03 ± 7.75	− ± −	0.02 ± 0.04
26	0.64 ± 0.19	180.28 ± 9.94	0.52 ± 0.10	1.11 ± 0.06	2260.16 ± 237.52	139.61 ± 11.27	0.33 ± 0.02	37.80 ± 4.83	232.60 ± 17.79	35.94 ± 7.68	0.20 ± 0.25	0.08 ± 0.07
30	0.93 ± 0.08	168.85 ± 31.75	0.49 ± 0.08	1.37 ± 0.31	2316.52 ± 80.22	149.40 ± 4.41	0.36 ± 0.05	37.70 ± 4.23	239.31 ± 17.95	27.67 ± 3.63	0.45 ± 0.50	0.37 ± 0.26
32	0.83 ± 0.21	142.81 ± 17.84	0.52 ± 0.09	1.41 ± 0.10	2412.34 ± 102.06	151.22 ± 0.07	0.40 ± 0.04	40.00 ± 4.44	247.11 ± 19.11	26.08 ± 2.83	0.33 ± 0.21	0.04 ± 0.07
34	0.75 ± 0.08	107.72 ± 13.44	0.44 ± 0.15	1.41 ± 0.30	2125.49 ± 407.11	130.27 ± 20.80	0.33 ± 0.12	35.13 ± 4.94	217.28 ± 17.80	22.83 ± 2.58	0.41 ± 0.33	0.09 ± 0.10
37	0.94 ± 0.13	82.96 ± 7.45	0.47 ± 0.07	1.67 ± 0.74	2611.34 ± 136.89	140.33 ± 3.03	0.39 ± 0.14	51.21 ± 0.89	251.96 ± 14.86	30.29 ± 1.47	− ± −	− ± −
39	0.96 ± 0.18	102.99 ± 14.36	0.55 ± 0.05	1.58 ± 0.35	3020.46 ± 108.74	167.92 ± 3.41	0.50 ± 0.06	62.01 ± 4.71	301.55 ± 20.96	39.25 ± 5.32	0.28 ± 0.19	0.02 ± 0.04
41	1.18 ± 0.07	77.66 ± 11.22	0.63 ± 0.11	1.49 ± 0.07	3170.31 ± 265.09	157.96 ± 16.23	0.36 ± 0.05	60.69 ± 4.60	307.64 ± 42.35	42.58 ± 6.43	0.90 ± 0.03	0.17 ± 0.05
44	1.33 ± 0.22	57.01 ± 2.99	0.64 ± 0.07	1.98 ± 0.17	3574.70 ± 114.72	161.47 ± 21.79	0.49 ± 0.09	79.04 ± 10.00	321.63 ± 21.79	61.11 ± 2.82	0.93 ± 0.58	0.15 ± 0.15
48	2.54 ± 1.69	60.57 ± 12.57	0.52 ± 0.04	1.63 ± 0.19	3413.45 ± 298.75	163.98 ± 1.21	0.41 ± 0.04	77.82 ± 0.87	283.27 ± 73.01	67.75 ± 0.05	0.71 ± 0.49	0.18 ± 0.04

[a] Data are the average of three fruits from one harvest and are expressed as mean ± standard deviation for each measurement.

directly or indirectly contribute to the combination of taste and aroma that characterizes high quality fruit.

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