TLC of the residue upon evaporation indicated that no other spots but the C_{22}-5-HT spot were apparent in this LC peak. Further work is required for the development of this method in roasted and ground coffee samples.

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Fatty Acid Profiles of Three Sweet Orange Cultivars during Maturation

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Total lipid fatty acid profiles for Hamlin (early ripening), Pineapple (midseason ripening), and Valencia (late ripening) oranges were examined monthly over an 11-month growing period. Purified total lipid extracts were separated into neutral lipid, glycolipid, and polar lipid fractions, and each fraction, in turn, was analyzed for fatty acids. Fatty acid profiles were also obtained for the triglyceride and sterol ester fractions for the months of September (immature fruit) and April (mature fruit). Fatty acid analyses by GLC revealed three periods, or stages, in the maturation of the cultivars. The period of greatest change occurred between July and the end of October; and the rate of change was greatest for Pineapple, next for Hamlin, and lastly, Valencia. Following this early rapid-change period was a 3- to 5-month middle period of relative inactivity (rates of changes were noticeably lower). The late (senescent) period, which then ensued, showed accelerated rate changes for the major fatty acids. Each of the three orange cultivars showed different fatty acid profiles at their respective maturation dates.

In previous publications we studied the lipids of citrus fruits with two main objectives. The first objective was to observe whether any relationship existed between lipids and off-flavor production during high-temperature storage of citrus products (Nagy and Nordby, 1970). The second objective was concerned with the possibility of utilizing lipids as chemotaxonomic markers (Nordby and Nagy, 1974). Our most recent objective is concerned with the relationship of lipids to the maturity of citrus fruits. To this end, we initiated studies on hydrocarbon changes in juice sacs during sweet orange maturation (Nordby and Nagy, 1977) and, more recently, showed that quantitative changes occurred in the neutral lipid, glycolipid, and polar lipid fractions of sweet oranges during an 11-month maturation period (Nagy et al., 1978).

Information on changes in fatty acids during fruit maturation is quite limited. Galliard (1968) presented profiles for apples during pre- and postharvest periods. Other fruits studied at two or three maturation periods include banana (Goldstein and Wick, 1969), pear (Romani et al., 1965), tomato (Kalra and Brooks, 1973), and mango (Gholap and Bandyopadhyay, 1975).

We undertook to determine the fatty acid profiles of sweet oranges during their maturation. Citrus fruits are distinct from the above fruits in that they will only ripen on the tree. Also, various citrus cultivars within the same species mature at different periods during the year, e.g., Hamlin, November–December; Pineapple, Janurary–February; and Valencia, March–April in Florida. In our study with hydrocarbons (Nordby and Nagy, 1977) "transition periods" corresponding to these cultivars ripening months were observed. Our objective of this study was to determine whether fatty acid profiles showed similar "transition periods".

EXPERIMENTAL SECTION

Fruit which set in February or March 1971 were collected monthly from July 1971 to May 1972. Cultivars examined were Hamlin (early season, November–December), Pineapple (midseason, January–February), and Valencia (late season, March–April) at the USDA Whitmore Experimental Farm (Crops Research Division, Orlando, Fla.). The preparation and storage of the freeze-dried juice powders, extraction–purification of the lipids, and fractionation of these extracts into three lipid classes were presented previously (Nordby and Nagy, 1977; Nagy

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Table I. Relative Percentages of Major Fatty Acids in Total Lipids of Three Orange Cultivars at 11 Stages of Maturity

	16:0			16:1			18:1			18:2			18:3		
month harvested	H[a]	P[a]	V[a]	H	P	V	H	P	V	H	P	V	H	P	V
Jul	25.8	24.5	25.3	3.7	4.0	2.7	20.0	20.4	17.9	37.8	42.1	43.7	11.4	8.6	9.5
Aug	25.2	23.9	25.6	4.3	5.7	3.7	25.5	25.7	20.8	34.7	37.2	41.6	9.3	7.0	7.5
Sept	23.2	23.1	25.3	4.4	6.4	4.7	29.6	29.5	22.6	32.7	34.1	39.9	9.2	6.4	6.7
Oct	23.5	22.4	24.9	4.1	5.6	6.0	29.8	32.0	27.6	32.3	31.7	34.1	9.5	7.8	6.7
Nov	23.0	22.2	22.6	3.6	5.5	6.0	27.6	31.8	29.7	30.1	30.0	33.9	14.9	9.9	7.2
Dec	22.7	21.5	22.9	3.7	6.1	6.1	28.4	31.6	30.5	28.1	29.6	32.9	16.3	10.6	7.0
Jan	23.4	20.9	21.0	3.8	5.3	5.9	29.9	31.4	32.4	24.8	28.4	32.0	17.2	13.3	8.0
Feb	23.7	21.5	21.8	3.3	5.3	5.9	28.4	30.9	32.9	24.5	27.4	30.9	19.3	14.4	7.7
Mar	26.4	22.2	22.4	4.1	4.3	4.3	27.0	30.5	33.1	21.8	25.7	30.3	19.9	16.6	9.0
Apr	26.7	22.5	22.1	4.3	6.4	4.5	26.6	29.5	34.8	20.8	24.7	29.5	20.8	16.4	8.2
May	26.0	22.3	22.6	3.3	5.4	4.6	25.9	29.6	33.7	24.4	25.2	28.7	18.5	16.3	9.6
mean	24.5	22.5	23.3	3.9	5.5	4.9	27.1	29.4	29.1	28.4	30.6	33.9	15.1	11.6	8.0
variation range[b]	4.0	3.6	4.6	1.1	2.4	3.4	9.9	11.6	16.9	17.0	17.4	15.0	11.6	10.2	2.9

[a] Hamlin, Pineapple, and Valencia cultivars, respectively. [b] Difference between lowest and highest values reported for this maturation period.

Table II. Relative Percentages of Major Fatty Acids in Neutral Lipids of Three Orange Cultivars at 11 Stages of Maturity

	16:0			16:1			18:1			18:2			18:3		
month harvested	H	P	V	H	P	V	H	P	V	H	P	V	H	P	V
Jul	19.1	19.0	16.1	6.2	6.5	4.9	20.2	18.2	17.3	34.6	38.8	44.0	11.8	10.5	12.4
Aug	18.8	17.6	14.4	6.1	7.5	6.8	25.8	25.6	19.2	34.2	35.0	43.4	8.6	7.6	10.3
Sept	19.5	18.1	15.8	5.9	8.0	8.0	29.8	30.8	23.4	29.9	30.1	39.7	8.2	5.9	7.4
Oct	15.6	14.7	13.9	5.9	9.1	9.9	28.7	29.9	25.6	31.9	30.9	36.6	12.1	8.5	7.6
Nov	15.2	14.4	12.7	5.2	7.6	9.0	25.7	30.6	28.4	29.1	30.3	35.0	19.1	11.9	8.3
Dec	14.0	11.3	12.1	5.3	7.9	9.1	25.6	28.9	30.3	27.8	31.9	33.1	22.8	15.0	7.3
Jan	14.4	12.5	12.1	4.9	7.1	8.0	26.6	30.0	33.0	25.4	29.7	31.6	24.1	15.8	8.6
Feb	13.4	12.5	11.8	5.7	6.3	8.1	26.9	28.8	31.5	25.6	28.7	32.3	25.2	18.6	9.8
Mar	16.2	13.0	10.0	5.4	6.9	8.5	23.6	29.3	30.8	24.4	26.7	32.4	25.8	19.4	11.4
Apr	16.7	13.3	10.7	5.3	6.2	8.1	23.7	28.5	32.7	23.2	27.1	31.7	24.8	19.1	11.4
May	20.6	13.3	9.5	4.0	7.3	8.2	21.3	28.0	32.4	27.9	27.0	31.4	19.2	19.0	13.1
mean	16.5	14.7	12.7	5.4	7.2	8.3	25.1	28.0	28.1	28.6	30.5	35.3	18.6	13.8	9.9
variation range	7.2	7.7	6.6	2.2	2.9	4.2	9.6	12.6	15.7	11.4	12.1	12.4	17.6	13.5	5.7

Table III. Relative Percentages of Major Fatty Acids in Glycolipids of Three Orange Cultivars at 11 Stages of Maturity

	16			16:1			18:1			18:2			18:3		
month harvested	H	P	V	H	P	V	H	P	V	H	P	V	H	P	V
Jul	24.4	22.5	27.1	4.4	5.7	4.4	24.3	26.1	18.6	16.2	23.1	29.5	29.5	22.0	19.5
Aug	23.7	22.5	23.9	5.8	7.9	5.4	30.6	33.5	26.0	13.0	17.5	24.3	26.0	17.8	19.4
Sept	23.5	22.3	22.1	6.0	9.6	7.4	33.6	37.5	28.2	10.7	15.2	21.0	25.2	14.5	20.2
Oct	22.7	21.7	23.2	5.2	9.1	8.1	35.2	38.9	34.1	11.3	12.7	17.0	24.6	16.6	16.6
Nov	22.5	21.1	20.3	5.1	8.1	8.7	33.3	37.9	37.2	10.8	13.8	16.8	27.6	18.2	16.1
Dec	23.1	22.3	18.9	4.9	8.2	8.9	33.0	38.0	36.5	10.5	14.6	16.8	27.7	15.9	18.1
Jan	24.1	24.6	19.8	4.9	6.0	8.7	34.9	37.2	38.2	9.9	14.2	18.4	25.4	17.4	13.7
Feb	25.2	22.6	21.6	4.7	6.7	8.3	33.8	37.4	39.8	10.2	14.6	17.0	25.1	17.9	12.2
Mar	30.2	22.4	22.8	3.7	6.8	8.1	32.6	37.9	40.1	8.4	13.9	16.8	22.4	18.3	11.4
Apr	29.7	23.5	23.6	2.9	7.4	7.5	32.2	38.4	38.3	7.3	14.0	18.4	26.0	15.7	11.0
May	27.7	25.5	23.7	5.4	7.3	7.2	32.0	37.4	38.5	8.6	12.7	19.1	22.2	15.5	10.6
mean	25.2	22.8	22.7	4.8	7.5	7.7	32.3	36.4	34.3	9.8	15.1	19.6	25.6	17.2	14.9
variation range	7.7	4.4	8.2	3.1	3.9	4.5	10.9	12.8	21.5	8.9	10.4	12.7	7.3	7.5	9.6

et al., 1978). Completeness and purity of lipid class separation were monitored by thin-layer chromatography. Triglycerides and sterol esters were isolated from the neutral lipid fractions of the September and April samples by TLC (hexane–ethyl ether, 9:1) (Nordby and Nagy, 1974). Fatty acid methyl esters (FAME) were prepared from the total, neutral lipid, glycolipid, and polar lipid samples with BF_3–MeOH (Metcalfe et al., 1966). Triglycerides and sterol esters were transesterified with HCl–MeOH (Nordby and Nagy, 1971). FAMEs from the total lipids, neutral lipids, and glycolipids and from the sterol esters were purified by TLC before analysis. GLC analyses were performed on a 3 m × 6 mm glass column packed with 3% SP-1000 operated isothermally at 160 °C (Nordby and Nagy, 1974). Four samples of each cultivar were analyzed from juice sac powders obtained monthly for 11 months. The relative percent values are the means of these samples analyzed in quadruplicate.

RESULTS AND DISCUSSION

Tables I to IV show the relative percentages of the five major fatty acids found in the juices of Hamlin, Pineapple, and Valencia orange cultivars during an 11-month maturation period. Table I contains values for the total lipid while Tables II to IV contain values for the neutral lipid, glycolipid, and polar lipid fractions, respectively. As observed previously (Nagy and Nordby, 1970; Nordby and Nagy, 1971) in the neutral fraction the major acylated lipids were triglycerides and sterol esters; in the glycolipids they were esterified sterol glucosides, monogalactosyl diglycerides, and cerebrosides, and in the polar lipids (phospholipids) they were phosphatidyl choline, phosphatidyl ethanolamine, phosphatidyl inositol, and phosphatidyl serine. These three lipid fractions monitored by

Table IV. Relative Percentages of Major Fatty Acids in Polar Lipids of Three Orange Cultivars at 11 Stages of Maturity

	16			16:1			18:1			18:2			18:3		
month harvested	H	P	V	H	P	V	H	P	V	H	P	V	H	P	V
Jul	33.0	26.9	28.1	2.7	3.0	2.3	18.0	19.5	18.0	37.7	43.0	43.8	7.5	6.8	6.9
Aug	32.4	26.4	30.4	3.2	4.7	1.6	23.2	25.1	21.4	33.6	37.2	40.7	6.5	5.9	5.1
Sept	31.7	26.5	29.4	3.4	6.0	4.1	25.4	26.1	21.8	31.7	35.2	39.2	7.0	5.8	5.0
Oct	33.2	26.5	28.6	2.9	5.7	4.9	24.9	27.9	26.3	30.7	32.6	34.3	7.3	6.9	5.3
Nov	30.4	26.4	27.4	3.0	5.3	5.4	23.8	27.7	28.1	29.5	31.1	33.2	12.3	9.0	5.3
Dec	31.4	25.9	27.7	2.9	5.0	5.3	24.7	29.6	30.2	26.8	29.4	31.5	13.2	9.3	4.7
Jan	31.5	25.3	25.4	3.3	5.1	4.8	25.8	29.5	31.3	22.8	28.2	31.8	15.5	11.3	6.0
Feb	32.8	25.8	26.7	3.3	4.8	4.8	24.7	29.7	31.2	22.4	26.9	30.1	15.8	12.1	6.5
Mar	33.9	26.7	25.8	3.5	4.7	4.6	23.6	29.7	30.7	20.3	25.0	30.7	17.6	13.0	7.5
Apr	33.1	26.9	25.6	3.5	5.2	5.0	24.2	28.7	31.9	20.3	25.1	29.3	17.7	13.1	7.5
May	34.8	28.2	26.1	3.1	3.2	4.9	22.9	27.9	32.4	20.7	25.4	28.4	16.7	14.3	7.3
mean	32.1	26.5	27.4	3.2	4.8	4.3	23.9	27.4	27.9	27.2	30.8	33.5	12.5	9.8	6.1
variation range	4.4	2.9	5.0	0.8	3.0	3.8	7.8	10.2	14.4	17.4	18.0	15.4	11.2	8.4	2.8

Table V. Major Rates of Change of Fatty Acids during Two Stages of Maturation[a]

	fatty acid/cultivar														
	16			16:1			18:1			18:2			18:3		
stage	H	P	V	H	P	V	H	P	V	H	P	V	H	P	V
(1) Aug-Sept															
total lipid	(2)[b]	(1)	c		2	1	8	8	4	(4)	(7)	(3)	(2)	(2)	(2)
neutral lipid					1	2	8	11	5	(4)	(7)	(3)	(3)	(4)	(4)
glycolipid			(4)	1	4	2	8	10	9	(5)	(7)	(7)	(4)	(6)	(1)
polar lipid	(2)		1		2	1	6	6	3	(5)	(7)	(4)			(1)
(2) Oct-Mar															
total lipid									1	(3)	(1)	(1)	3	2	
neutral lipid			1				(1)			(2)		(1)	4	3	1
glycolipid	2								1						(1)
polar lipid									1	(3)	(2)	(1)	2	1	

[a] Rates of change rated on a scale of 0.02% change/day equal to a value of one beginning at 0.021%/day. [b] Values in parentheses show decreasing rates. [c] Rate of change less than 0.021%/day.

TLC were observed not to overlap. Preliminary analyses showed C_{10} to C_{15} and C_{20} to C_{26} fatty acids present in limited quantities only in the neutral lipid fraction. With the exceptions of lauric (12:0) and myristic (14:0) acids, all other minor acids in the C_{10} to C_{15} range were found at percentages less than 0.5% and, therefore, were excluded from this study. Fatty acids in the C_{20} to C_{26} region did not show any significant changes during maturation and, thus, were also excluded from Table I to IV. Fatty acids included in the calculations but not presented in Tables I to IV are lauric, myristic, and stearic acids. The first two acids were present in the neutral lipid fractions of the three cultivars at relatively constant levels of 1.8% (lauric) and 2.7% (myristic) over the 11 months. Stearic acid was present in all three fractions at less than 1.2% for the first 6 months. During the last 3 months the percentages rose from 1 to 2% in the neutral lipid fractions and slightly more in the glycolipid fractions, e.g., to 4.2% (Hamlin), 1.6% (Pineapple), and 1.0% (Valencia).

Tables I to IV reveal that changes in the percentages of the fatty acids were substantial during the first 3 months of sampling, not very marked over the next 6 months, and again substantial over the last 2 months. These three periods appeared to correspond to three stages of maturation and, the changes seemed linearly related to time of sampling. To quantify these differences we subjected the data to regression analyses. Since the initial July samples were collected near the end of that month, regression analyses were calculated for the stages August 1 to September 30, October 1 to March 31, and April 1 to May 31. The results of the analyses for the first two stages are summarized in Table V. The slope of each regression line within each of the two stages represents a percentage rate of change. These rates of change were placed on an 11-point scale. Rates 0 to 0.02%/day were considered negligible and are labeled with a dash. Rates 0.021 to 0.040%/day were given a scale rating of 1, rates 0.041 to 0.06 a rating of 2, rates 0.061 to 0.08 a rating of 3, etc. Under this system percentage rates of change of 0.056 and 0.168%/day would have scale values of 2 and 8, respectively. Decreasing rates of change are indicated by parentheses.

From July to October, orange fruit exhibit weight gain (Harding et al., 1940), cellular enlargement (Bain, 1958), and enhanced phospholipid formation (Nagy et al., 1978). During stage 1 all three orange cultivars showed large percentage changes in 18:1, 18:2, and 18:3 and only moderate changes in 16:0 and 16:1. During stage 1, 16:0, 18:2, and 18:3 decreased while 16:1 and 18:1 increased. The data for the C_{18} acids strongly suggest enzymic reduction of the 18:2 and 18:3 acids to 18:1.

During stage 2, the rates of change were greatly reduced from those of stage 1. Maximum scale number (rate of change) was 4 in stage 2 (Hamlin neutral lipid) and 11 in stage 1 (Pineapple neutral lipid). In stage 2 total lipid 18:2 decreased at about the same rate that 18:3 increased. The major changes during stage 2 were in the neutral and polar lipid fractions. In the neutral lipid fraction 18:3 increased over a 6-month period at rates of 0.094, 0.073, and 0.023%/day (e.g., scale numbers 4, 3, 1) for Hamlin, Pineapple, and Valencia, respectively. During later months (April and May, stage 3 not recorded in Table V), 18:3 decreased in Hamlin (0.118%/day) and in Pineapple (0.007%/day) but increased continuously in Valencia (0.023%/day).

Banana pulp (Goldstein and Wick, 1969) and mango pulp (Gholap and Bandyopadhyay, 1975) show, upon ripening, an increase in 18:3 and a reduction in the relative percentages of 18:1 and 18:2. From our data we postulate that oranges are capable of synthesizing linolenic acid

(18:3) over the entire extensive growing period, thus reducing the relative levels of 18:1 and 18:2. In contrast, the pome fruit, apple (Galliard, 1968), shows a drastic decrease in 18:3 contents within the triglyceride and polar lipid fractions but only a minor decrease within the glycolipid fraction upon ripening.

Fatty acid profiles of triglycerides in mature citrus fruit have been published (Nordby and Nagy, 1971; Nagy and Nordby, 1974). In September, the 18:3 contents of the neutral lipids for Hamlin, Pineapple, and Valencia were lowest (Table II), i.e., 8.2, 5.9, and 7.4%, respectively. These percentages for the neutral lipid fractions agreed quite closely with triglyceride 18:3 values for September, viz., 11.1, 6.8, and 9.7%, for Hamlin, Pineapple, and Valencia, respectively. These triglyceride values were below those reported for mature orange (Nordby and Nagy, 1971). In April, the three orange cultivars had triglyceride 18:3 values of 30.2, 22.4, and 14.7%; these compared favorably to the corresponding neutral lipid 18:3 values (Table II). The triglyceride values for April were higher than those reported for mature Hamlin and Pineapple oranges but slightly lower than the reported Valencia value. The triglycerides were analyzed in September because then the fruit are immature [low 18:3 value; low Brix/acid ratios (Nagy et al., 1978); low juice volume (Harding et al., 1940)] and in April, because the fruit are either mature (Valencia) or overripe (Hamlin and Pineapple).

Relative percentages of sterol esters (SE) 18:3 in the three orange cultivars during September and April were, respectively, Hamlin, 39.1 and 38.3%; Pineapple, 8.0 and 26.6%; Valencia, 6.5 and 9.9%. Although the percentage of SE 18:3 in Hamlin during September was high, the percentage in the neutral lipid fraction was only 8.2%. This indicates that SE 18:3 does not substantially influence the overall 18:3 level in the neutral lipid fraction. The analyses of SE 18:3 indicates that the fatty acid percentages in Hamlin SE do not change much between September (immature) and April (overripe). The lack of extensive change in Hamlin SE is further substantiated by the fact that percentage values for 16:0, 16:1, 18:0, 18:1, and 18:2 varied by less than 2% between September and April. The difference between Pineapple SE 18:3 values during these 2 months indicates a juvenile fatty acid pattern in September and a mature pattern in April. In Valencia SE 18:3 changed about 3% between September and April. As compared to published SE profiles (Nordby and Nagy, 1971, 1974) of mature Valencia oranges, the SE fatty acid profile for April may still be regarded as that of immature fruit.

Upon fruit maturation the increase in triglyceride 18:3, which essentially caused the increased 18:3 in the neutral lipid fraction, contrasts with the reported large decline of 18:3 in apple triglycerides (Galliard, 1968). In citrus, glycolipids and polar lipids are associated with chromoplasts which develop from pigmentless plastids within the juice vesicles (Goldschmidt, 1977). With the exception of vesicular epicuticular wax (Fahn et al., 1974; Shomer and Ben-Gera, 1975), the location of neutral lipid components within the juice vesicle has not been established. Since 18:3 percentages increased substantially in triglycerides, it would be of interest to know the location and biochemical function of these triglycerides within the vesicle.

In noncitrus fruits the level of saturated fatty acids increases during the ripening process (Galliard, 1968; Goldstein and Wick, 1969; Romani et al, 1965). This appears to happen in citrus as well, since both 16:0 and 18:0 increased with time (data not shown). The increase in saturated fatty acids within the glycolipid fraction of oranges during ripening (Tables III and V) agrees with reported increases in 16:0 and 18:0 in noncitrus fruits.

Table VI. Relative Percentages of Fatty Acids in Three Orange Cultivars at Their Respective Maturation Dates[a,b]

lipid fraction	16:0	16:1	18:1	18:2	18:3
total lipid					
Hamlin	23.0	3.9	29.0	29.9	13.1
Pineapple	22.5	5.4	31.3	28.9	11.8
Valencia	21.9	4.9	33.0	30.5	8.4
neutral lipid					
Hamlin	16.0	5.5	26.9	29.6	16.3
Pineapple	11.8	7.4	29.5	31.5	14.3
Valencia	10.9	6.5	31.0	32.4	10.7
glycolipid					
Hamlin	22.4	5.3	34.3	10.6	26.4
Pineapple	22.7	7.2	38.0	13.8	17.1
Valencia	22.0	8.0	38.6	17.9	12.4
polar lipid					
Hamlin	30.4	3.0	24.9	28.7	10.7
Pineapple	25.8	5.2	29.9	29.5	9.9
Valencia	26.2	4.9	31.4	29.9	6.7

[a] Determined from linear regression plots. [b] Maturation dates (Nordby and Nagy, 1977) are Hamlin, Nov 27; Pineapple, Jan 12; Valencia, Mar 28.

For mangoes use of the ratio 16:0/16:1 (Gholap and Bandyopadhyay, 1975) as an index of maturity is due to the rapid increase in 16:1 during the ripening process. This ratio, however, could not be applied to citrus since 16:1 percentages remain rather static from September through the remainder of the growing period.

As evident from Table V and data on citrus lipid classes (Nagy et al., 1978), the three orange cultivars metabolize fatty acids at different rates. At their respective maturity dates, all three cultivars might be expected to have similar fatty acid profiles. As reported previously, the maturity dates of the cultivars were determined on the basis of a Brix/acid ratio of 12.0 (Nordby and Nagy, 1977). The dates at which each cultivar reached the 12.0 ratio were: November 27 (Hamlin), January 12 (Pineapple), and March 28 (Valencia). From linear regression, we determined the fatty acid percentages for each cultivar at their respective maturity dates (Table VI). Each cultivar showed its own intrinsic fatty acid profile. The cultivars appeared to be noticeably different in their 18:1 and 18:3 percentages of the total and the neutral lipid fractions. They also differed in values for 18:2 and 18:3 of the glycolipid fraction and in 18:1 of the polar lipid fraction.

From fruit-set to maturity, growth of sweet oranges pass through three well-defined stages (Bain, 1958), viz. (a) rapid cell division, (b) cell enlargement, and (c) maturation. The maturation stage (includes the ripening period) is characterized by reduced respiration and by constant slow compositional changes [e.g., reduction in citric acid, increase in Brix/acid values (Harding et al., 1940)]. As evidenced by a gradual uniform decline in respiration, there appears to be no clear demarcation between fruit ripeness and onset of senescence (Bain, 1958).

The results of this study clearly point out differences in maturation characteristics between citrus fruit specifically *C. sinensis* and other common fruits. Metabolic changes in lipids within the fruit from the time of fruit set to July was not studied and data therefrom can only be inferred from profiles of the three cultivars during the months of August, September, and October. During these months rapid changes occurred in all three cultivars although not at the same rate. Rates were greatest for Pineapple, less for Hamlin, and least for Valencia. In the second stage, rate differentials appeared to correlate with the sequence in which these cultivars mature. Enzymes

associated with the synthesis of linolenic acid appeared to be active throughout the growth period of each cultivar. Although we previously showed hydrocarbon profiles of these three orange cultivars to correlate closely with dates of ripening (Nordby and Nagy, 1977), the present study showed no definitive correlation between these cultivars fatty acid patterns and ripening dates.

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Volatiles of Wild Strawberries, *Fragaria vesca* L., Compared to Those of Cultivated Berries, *Fragaria* × *ananassa* cv. Senga Sengana

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Volatile components of Finnish wild strawberry, *Fragaria vesca* L., and of cultivated strawberry, *Fragaria* × *ananassa* cv. Senga Sengana, were studied by combined gas chromatography–mass spectrometry. In all, 87 compounds were identified in the wild and 58 in the cultivated berries. 2,5-Dimethyl-4-methoxy-3(2*H*)-furanone was identified as the main volatile component in the berries of *F. vesca* L. and as an abundant component also in the cultivated berries. Other compounds reported here for the first time as strawberry volatiles include 3-methyl-2-butenyl acetate, methyl nicotinate, carveyl acetate, methyl anthranilate, methyl *N*-formylanthranilate, verbenone, citronellol, myrtenol, 6-methyl-5-hepten-2-ol, eugenol, vanillin, 2-methoxy-4-vinylphenol, and 4-vinylphenol.

The volatiles of cultivated strawberries have been very extensively studied during the last 25 years. Winter and Willhalm (1964) identified over 60 compounds in *Fragaria* × *ananassa* (var. Surprice des Halles) including *trans*-2-hexen-1-ol, 2-ethylhexanol, 2-hexenal, hexyl acetate, *trans*-2-hexenyl acetate, ethyl butyrate, ethyl acetoacetate, and α-terpineol. Later the same authors (Willhalm et al., 1966) reported that the main volatile acids of strawberries consisted of 2-methylbutanoic, hexanoic, and 2-methylpropanoic acids.

McFadden et al. (1965) reported the identification of *cis*- and *trans*-3-hexenyl hexanoates, *trans*-2-hexenyl hexanoate, linalool, and several other compounds not reported previously as constituents of strawberry aroma. Tressl et al. (1969) identified about 200 compounds in the berries of the cultivar Revata. The main components included such previously unidentified compounds as octyl butanoate, octyl 2-methylbutanoate, octyl hexanoate, and γ-dodecalactone. Stoltz et al. (1970) identified 1,2-dihydro-1,1,6-trimethylnaphthalene in strawberry oil and Mussinan and Walradt (1975) found over 20 volatile acids which had not previously been identified in strawberries.

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In a recent study Dirinck et al. (1977) used headspace concentration on Tenax to evaluate the aroma quality of cultivated strawberries. They identified about 30 volatiles eluting before *n*-undecane in a SE-30 capillary column.

The over 60 esters, 30 alcohols, and about 30 carbonyl compounds identified in these studies do of course contribute to the estery and green notes of the odor of strawberries, but they can hardly be considered to contain a "character-impact" compound or compounds. Sundt (1970), however, has reported the identification of 2,5-dimethyl-4-hydroxy-3(2*H*)-furanone in strawberries, and this compound may well be considered the most important aroma constituent of strawberries so far reported.

Drawert et al. (1973) and Staudt et al. (1975) compared the volatiles of the berries of several wild strawberry species with those of the cultivar Revata. The wild berries of species *F. vesca* L. and *F. moschata* L. were shown to contain high amounts of 2-alkanones and 2-alkanols, most of which have not been identified in or are only minor constituents of cultivated berries. On the other hand, fewer esters of aliphatic carboxylic acids and no hydrocarbons were identified among the volatiles of the wild berries.

The odor of Finnish wild strawberry is more herbaceous and markedly stronger than that of cultivated strawberry. The 2-alkanones and 2-alkanols previously identified in

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