Effect of Nitrogen and Potassium Fertilization on Tomato Flavor

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Tomato plants were treated with three levels of nitrogen (N) and potassium (K) to determine whether fertilization practices influence tomato flavor as determined by sensory analyses and the measurement of soluble solids, pH, titratable acidity, and volatile constituents. Gas chromatography (GC) retention times and mass spectrometry (MS) were used to identify volatile compounds whose concentrations changed with fertilization treatments. Flavor scores indicated that increased nitrogen and potassium fertilization had a detrimental effect on tomato flavor. An increase in titratable acidity and soluble solids was found with increasing fertilization. Concentrations of hexenal, 2-hexanone, benzaldehyde, phenylacetaldehyde, β-ionone, and 6-methyl-5-hepten-2-one increased with increasing N–K levels.

INTRODUCTION

The increasing adoption of precision growing techniques in the horticultural industry is necessitating more detailed studies of the factors controlling fruit and vegetable quality. Although tomatoes are an important agricultural commodity, little is known about the growing conditions that influence the flavor of tomatoes. Much popular concern has been expressed regarding the deteriorating quality of tomatoes available in the consumer market (Harris, 1973; Cerra, 1975) and while much of the blame has been laid on new varieties, it is apparent that degree of ripeness also has an effect. Kadar et al. (1977) reported that tomatoes picked at underripe stages were less sweet, more sour, less "tomato like" and had more off flavor than those at the table ripe state. Shah et al. (1969) demonstrated that long-chain carbonyls and terpene esters are essential for ripe tomato aroma. The extent to which growing conditions may affect tomato flavor is not known.

The flavor properties of tomato fruits are determined largely by the amount of sugar, the organic acid content, and the volatile compound composition. Simandle et al. (1966) found taste panel flavor scores to be significantly correlated with soluble solids and soluble solids/titratable acidity ratio. DeBruyn et al. (1971) concluded that high sugar and high acid contents generally have a favorable effect on taste. Davies and Winsor (1967) have demonstrated decreased sugar content of tomato fruit when nitrogen fertilization is increased.

The predominant acid of ripe tomato fruit is citric with malic the next most abundant (Carangal et al., 1954). Not only are the organic acids important as major taste components, but total acidity plays an important part in the satisfactory processing of tomato products (Lambeth et al., 1964; Bisogni and Armbruster, 1976). Highly significant positive correlations have been reported between potassium content of the growing medium and titratable acidity (Davies, 1964; Sakiyama, 1966). The acidity of the tomato is also increased by nitrogen in the soil. No previous research has been conducted to determine the effects of fertilizer regimes on flavor and volatile components of tomatoes. It was the purpose of this research (1) to determine whether the concentration of nitrogen and potassium used in fertilizing tomato plants affects the flavor of the tomato and (2) to discover whether there are any changes in the soluble solids, pH, titratable acidity, or in the kinds and amounts of volatile flavor constituents in tomatoes that have received varying nitrogen and potassium treatments.

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EXPERIMENTAL SECTION

Growth Conditions. Tomato plants (Walter cv.) were grown on trellis and plastic mulch at the Agricultural Research and Education Center of the University of Florida in Quincy. Nitrogen and potassium fertilization treatments were administered by means of a trickle irrigation system at one-week intervals for 15 weeks. Treatments consisted of (I) 100 lb/acre (1b/A) of nitrogen and 150 lb/A of potassium, (II) 200 lb/A of nitrogen and 300 lb/A of potassium, and (III) 300 lb/A of nitrogen and 450 lb/A of potassium. All plots received 200 lb/A of P_2O_5 initially. These treatments constituted a 4-0-6 (N–P–K) ration administered as KNO_3, NH_4NO_3, and water. Each treatment group contained 90 plants.

Sampling. Tomatoes were harvested at the firm, full red, table ripe stage and stored no longer than 2 days at 4 °C. Three 5-kg tomato samples were chosen at random from each treatment after harvest. Each sample was macerated in a Waring blender for 1 min and frozen in pint jars at −20 °C. Samples were held at −20 °C until aliquots were drawn for determination of soluble solids, pH, titratable acidity, percent moisture, volatiles and for sensory analysis.

Soluble Solids, Titratable Acidity, Percent Moisture, and pH. Soluble solids content was determined with a Bausch and Lomb Abbe 3L refractometer corrected for temperature at 25 °C. To determine titratable acidity, 10-g aliquots were weighed into 250-mL beakers, in triplicate, and diluted with 150 mL of distilled water. The diluted sample was agitated mechanically and titrated with 0.1 N NaOH to a pH value of 8.1. The results are expressed as percent citric acid. pH was determined with a Corning pH meter equipped with a glass-calomel electrode. Percent moisture was determined by drying a series of 5-g samples to constant weight in a drying oven at 100 °C.

Volatiles. Fresh ripe tomatoes were blended as described above and a 1-kg aliquot was then treated in a steam distillation continuous extraction apparatus (Nickerson and Likens, 1966), with the product held at 100–110 °C. Three extractions were performed on each treatment. Hexane was the extracting solvent and condensors were cooled with ice water. The extraction was carried out over a 3-h period after which the hexane extract was dried over anhydrous sodium sulfate and filtered, and the solvent removed in a rotaty evaporator to yield the tomato oil concentrate. After evaporation, 0.05 mL of decanal was added to the extract as a reference compound for peak areas. Tomato concentrate samples were kept at −12 °C

0021-8561/85/1433-0355$01.50/0

Table I. Influence of Nitrogen and Potassium Levels on Titratable Acidity, pH, and Soluble Solids of Tomatoes

N/K treatments (N/K, lb/A)	titratable acidity, % citric acid	pH	soluble solids, %	% moisture
100/150	0.499 ± 0.11[a]	4.22 ± 0.3[a]	5.48 ± 0.21[a]	92.7 ± 0.8[a]
200/300	0.554 ± 0.07[b]	4.27 ± 0.02[a,b]	5.82 ± 1.11[b]	93.1 ± 0.7[a]
300/450	0.618 ± 0.010[c]	4.20 ± 0.02[b]	6.21 ± 0.20[c]	92.5 ± 0.6[a]

[a] Data in a column followed by different letters are statistically different at the $\alpha = 0.05$ level of significance. Values are means of four determinations for all tests except soluble solids where data are means of six determinations.

until gas chromatographic (GC) analysis. Between GC injections, the vials containing tomato concentrate were kept on ice.

GC Methods. Samples of tomato concentrate were analyzed on a Varian Model 3700 gas chromatograph with a flame ionization detector. The column was a 25 m OV-101 glass capillary column (Varian). The programming sequence consisted of a 3-min post-injection interval at 60 °C followed by programming at 5 °C/min to 190 °C and a 1-min interval at final temperature. Injection port and detector temperatures were 240 °C. The nitrogen flow rate was 30 mL/min. Peak areas are reported as the ratio of each peak area to the reference area. Retention time was used to tentatively identify those compounds that varied with treatments. Compounds whose ratios varied significantly among treatments were further analyzed by gas chromatography–mass spectrometry (GC–MS) and comparisons made of mass spectra of standard compounds and those of tomato concentrate unknowns.

GC–Mass Spectrometry. GC–mass spectra were obtained with a Finnigan 4510 GC Mass Spectrometer equipped with a INCOS data reduction system. Samples were introduced by on column injection (J & W Scientific). The chromatography column was a 30M DB-5 fuse silica capillary column which was passed directly through a vacuum interlock into the ion source. The carrier gas was hydrogen. After sample injection the GC temperature was raised from 60 to 140 °C at 30 °C/min. The temperature was then linearly programmed to 240 °C at 50 °C/min. Mass spectra were recorded once every second. The electron energy was 70 eV. The ion source pressure was less than 5×10^{-6} torr for these electron ionization experiments.

Taste Panel Methods. Sixteen panelists were selected for their ability to distinguish between tomato puree from overripe tomatoes and ripe tomatoes. Those selected were further trained to detect differences in tomato flavor and to use the scoring scale. A hedonic scale (1–10) was used to evaluate tomatoes for flavor. A score of 1 indicated not acceptable while 10 indicated very acceptable. No descriptive terms to describe flavor were elicited from the panel. Flavor evaluations were held in midafternoon in a clean, quiet, well-ventilated room. The room was dimly lit so that panel members would not be influenced by sample color and panelists were reminded to judge the samples solely on the basis of flavor. Samples were thawed at 8 °C for 24 h and then were raised to room temperature, approximately 25 °C, for presentation to the panel.

Statistical Analysis. For soluble solids, titratable acidity, pH, volatiles, and percent moisture, a one-way analysis of variance was used to test the null hypotheses, i.e., no significant differences among the three treatment groups. The amount of volatile$_x$ was measured as the ratio of the area of peak$_x$ to the area of the standard peak (peak 16) × 100%. The arc sin transformation was used to normalize the ratios. A separate test was performed for each volatile across the three treatments.

RESULTS AND DISCUSSION

Flavor. Taste panel results indicated a significant difference in flavor between treatment I and treatment II and III at the $\alpha = 0.05$ level of signifiance. Mean flavor scores from three preference tests given to 16 panelists and scored on a 1–10 scale (1 = very unacceptable, 10 = very acceptable) were 6.5, 4.1, and 4.2 for treatments I, II, and III, respectively. Thus, tomatoes receiving the lower level of N–K fertilization were preferred for flavor.

Soluble Solids, Titratable Acidity, pH, Percent Moisture. Soluble solids content was found to increase with increasing levels of N and K (Table I), possibly as a direct result of the characteristic role of N in accelerating photosynthetic activity through increasing the amount of foliage, the quantity of chlorophyll, and ultimately the photosynthetic activity of the plant. Photosynthate produced beyond the amount needed for plant structure is stored as reducing sugars, the primary components of a soluble solids measurement.

Increased titratable acidity was associated with the higher levels of nitrogen and potassium (Table I). A slight trend toward lower pH values at lower fertilization levels was observed. It is generally accepted that titratable acidity and soluble solids are positively correlated with overall flavor acceptance. The higher fertilization levels in the present study resulted in higher titratable acidity and soluble solids but the sugar–acid ratio showed little change. Sugar–acid ratio values were 11.0, 10.5, and 10.5 for treatments I, II, and III, respectively, and may have had only a negligible, if any, influence on flavor. The data in this study lend support to Bisogni and Armbruster's (1976) postulate that additional components of tomatoes are apparently more influential in flavor quality of tomatoes than acidity or solids.

Volatiles. Tomato concentrate was analyzed by GC and MS to determine the effect of fertilization on relative amounts of hexane-extractable volatiles. Chromatograms from each of the treatments are shown in Figure 1. A total of eleven compounds were found to change quantitatively with fertilization treatment. Table II shows the peak ratio areas which differed significantly due to fertilization treatments.

The amount of hexenal was found to increase with increasing nitrogen and potassium fertilization. It was not possible to determine by GC and MS techniques whether peak 3 represents the cis or trans isomer of hexenal. *trans*-2-Hexenal is not present in the intact tissue but is produced by a sequence of rapid enzymatic reactions initiated by cellular disruption under aerobic conditions, possibly for antimicrobial defense (Kosuge and Yokota, 1963). Kazeniac and Hall (1970) reported that high speed blending for several seconds is sufficient to convert most of the *cis*-(*E*)-hexenal to the trans isomer. At levels of 1 ppm and higher, *cis*-3-hexenal produced strongly "green" rancid-type flavors which werre found to be objectionable. It is possible that the cis isomer of hexenal contributed to undesirable flavors at the levels present in this study.

The increase in 2-hexanone (peak 2) and 2,4-hexadienal (peak 6) observed with increasing levels of nitrogen fertilization supports the theory that short-chain carbonyls are synthesized from amino acids in the tomato. Y (1967) observed that crude enzyme preparations from green to-

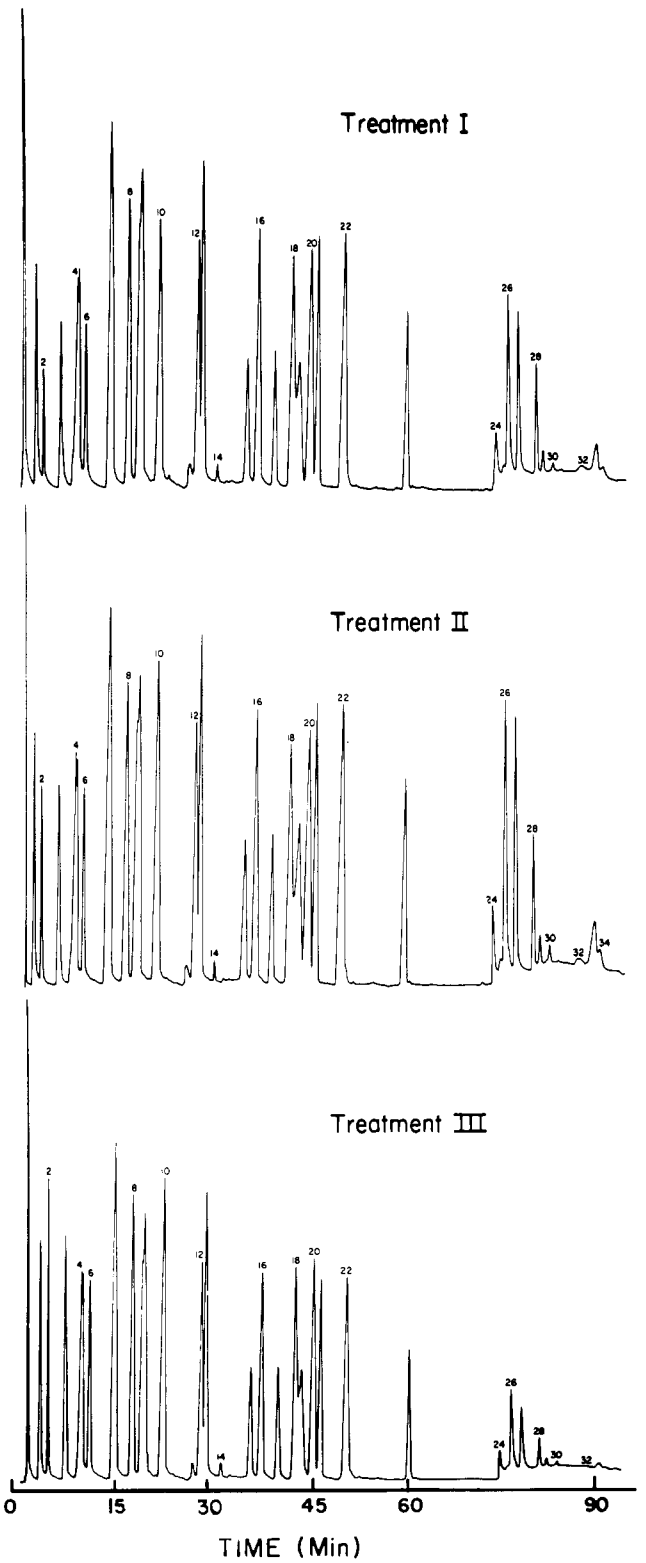

Figure 1. Gas chromatograms of tomatoes grown with different fertilization treatments: Treatment I = 100 lb/acre of nitrogen and 150 lb/acre of potassium. Treatment II = 200 lb/acre of nitrogen and 300 lb/acre of potassium. Treatment III = 300 lb/acre of nitrogen and 450 lb/acre of potassium. Peak ratio areas which were significantly different ($p < 0.05$) are identified in Table II. GLC conditions are described in text.

matoes synthesized short-chain carbonyls, especially C_6 moieties, when alanine, leucine, and valine were used as substrates. As the fruit ripens, more intricate enzyme systems become operative and utilize several kinds of substrates in the process of synthesizing volatile compounds. Under high nitrogen conditions, the concentrations of these short-chain carbonyls may increase to a level that masks desirable compounds that contribute to ripe tomato flavor.

The concentrations of benzaldehyde (peak 7) and phenylacetaldehyde (peak 10) were higher in tomatoes from the high nitrogen and potassium treatment than tomatoes from the low fertilization treatments. The relatively large amounts of these two compounds found in this study as compared to the smaller amounts found by Buttery et al. (1971) and Kazeniac and Hall (1970) may be a result of the heat produced during the atmospheric steam distillation. Heat can convert mandelic acid or phenylglyoxylic acid to benzaldehyde. Benzaldehyde has a high threshold (Buttery et al., 1971) so it probably has little effect on flavor. On the other hand, phenylacetaldehyde has a low threshold and small quantitative differences would be expected to affect flavor. At concentrations as low as 0.5 ppm it can loose its typical floral note and develop undesirable flavors in tomato juice (Kazeniac and Hall, 1970).

Kazeniac and Hall (1970) found phenylacetaldehyde to be produced at a fairly constant though low rate during the atmospheric steam stripping of volatiles from tomato homogenates or pulp. According to Shah et al. (1969), the origin of benzaldehyde, phenylacetaldehyde, and other aromatic compounds in tomatoes could be traced back to shikimic acid, which is derived from erythrose-4-phosphate and pyruvic acid, both of which are intermediates of carbohydrate metabolism. Increased nitrogen and potassium fertilization may result in an overall increase in carbohydrate metabolism because of increased photosynthetic capability. Phenylalanine is thought to be the precursor of phenylacetaldehyde (Kazeniac and Hall, 1970). Meigh et al. (1966) showed that tomato tissues produced acetaldehyde, propanal, and acetone enzymatically from the corresponding alcohols.

The terpenoids β-ionone (peak 23) and 6-methyl-5-hepten-2-one (peak 8) were found to increase in concentration with nitrogen and potassium fertilization. However, concentrations of isomers of another terpenoid, farnesol (peaks 24, 26, 27, and 28), were greatest for treatment II and lowest in tomatoes from treatment III.

The biogenic isoprene rule of Ruzicka (1953) implies that all terpenoids have a common precursor. The biosynthetic pathway from acetate to mevalonate and finally to dimethyl allyl pyrophosphate, the common precursor, is well established, but it is also possible that dimethyl allyl pyrophosphate may in certain circumstances originate from other pathways, e.g., valine in bananas (Hultin and Proctor, 1962) and β-methylcrotonic acid in *Mentha pulegium* (Sandermann and Stockmann, 1958). Shah et al. (1969) have suggested that other isopentanes such as isoamyl alcohol, isovaleraldehyde, and others may act as precursors of terpenoids through dimethyl allyl pyrophosphate. Valine and leucine, the amino acids with an isopropyl group, could form terpenoids in a similar manner. This could account for the increase in β-ionone and 6-methyl-5-hepten-2-one in tomatoes with high nitroge fertilization.

Cole and Napur (1957) have isolated 6-methyl-5-hepten-2-one from lycopene degradation during the heating of tomato pulp. Oxygen availability was the most important factor in lycopene degradation. Thus, this compound may be an artifact but one whose increasing concentration with increasing nitrogen and potassium fertilization is representative of changes in some precursor compound, possibly lycopene or methylheptenol.

Table II. Peak Ratio Areas Which Differed Significantly due to Fertilization Treatments

peak	compd[a]	peak ratio area, mm^2,[b] fertilization treatments[c] I	II	III
2	2-hexanone	0.74 ± 0.15	1.10 ± 0.09	1.66 ± 0.14
3	hexenal	2.03 ± 0.12	2.50 ± 0.10	3.05 ± 0.05
6	2,4 hexadienal	2.57 ± 0.17	2.81 ± 0.14	3.28 ± 0.19
7	benzaldehyde	8.04 ± 0.05	8.54 ± 0.10	8.98 ± 0.08
8	6-methyl-5-hepten-2-one	5.64 ± 0.12	6.20 ± 0.04	6.6 ± 0.13
10	phenylacetaldehyde	5.55 ± 0.14	6.26 ± 0.08	7.40 ± 0.11
18	citral	5.07 ± 0.10	5.72 ± 0.04	5.41 ± 0.09
20	unknown	4.83 ± 0.13	5.61 ± 0.15	5.95 ± 0.12
22	eugenol	6.73 ± 0.09	7.21 ± 0.07	7.81 ± 0.07
23	β-ionone	2.94 ± 0.02	3.48 ± 0.04	3.79 ± 0.06
24	farnesol isomer	0.93 ± 0.10	1.20 ± 0.022	0.64 ± 0.05
26	farnesol isomer	2.51 ± 0.10	3.01 ± 0.08	1.94 ± 0.12
27	farnesol isomer	2.30 ± 0.02	2.90 ± 0.01	2.20 ± 0.04
28	farnesol isomer	0.92 ± 0.04	1.43 ± 0.01	0.50 ± 0.03

[a] Compounds were identified tentatively by retention time and comfirmed with mass spectrometry. [b] Area ratio of compound is significantly different among treatments at the $\alpha = 0.05$ level of significance. The above figures represent averages of three replications per treatment. [c] Treatment I = 100 lb/acre of nitrogen and 150 lb/acre of potassium. Treatment II = 200 lb/acre of nitrogen and 300 lb/acre of potassium. Treatment III = 300 lb/acre of nitrogen and 450 lb/acre of potassium.

The eleven compounds that changed quantitatively with fertilization treatment were tentatively indentified by retention time and then most were confirmed by mass spectrometry. However, mass spectral identification of peaks 18 and 20 was inconclusive. Peak 18 exhibited a retention time identical with citral under the GC conditions given above. Both 3,7-dimethyl-2-6-octadien-1-ol and 2-undecanone gave similar mass spectra to that of the sample. Peak 18 was greatest at treatment II levels of N and K. Peak 20 may have been either hexadecanol or undecanal as demonstrated by comparison with MS data. Peak 20 was found to increase with increasing N and K levels. Peak 22 exhibited similar retention behavior to eugenol (2-methoxy-4-(2-propenyl) phenol) and a close fit was observed with MS data for that compound. Although there is little research reported on the role of eugenol in plants, it appears to act as an antimicrobial agent. According to Buttery et al. (1971), it has a low threshold. Although there is no evidence of a relationship between eugenol production and nitrogen or potassium fertilization it was observed that the levels of this compound decreased with increasing fertilization.

From the results of this study, it appears likely that the undesirable flavor associated with high nitrogen and potassium fertilization levels are due to some factors other than the traditional flavor indicators of soluble solids and titratable acidity. The odors of the short-chain carbonyls, hexenal, 2-hexanone, and 2,4-hexadienal may contribute to the poor flavor of tomatoes from treatments II and III. It is difficult to draw conclusions from correlations of volatiles with flavor since no method of extraction is so mild as to not upset the pattern of volatiles present. It must be noted that samples analyzed chemically in this study were heated while those analyzed by the taste panel were not heated. It is possible that some changes in flavor compounds occurred during the chemical analyses.

Further research is needed for a more precise assessment of the role of the components identified. Although in the present study only relative concentrations of compounds were determined, actual concentrations of the compounds which were different in the three treatments should be determined so the data could be related to flavor thresholds. Also, the addition of the identified compounds to samples for sensory analyses could aid in determining the role of individual or groups of such compounds in tomato flavor. It is possible that research in this direction could result in high-yield agricultural techniques compatable with good flavor in tomatoes.

ACKNOWLEDGMENT

We wish to thank F. Rhoads, University of Florida Agricultural Research and Education Center, Quincy, FL, for supplying us with tomato samples.

Registry No. 2-Hexanone, 591-78-6; hexenal, 1335-39-3; 2,4-hexadienal, 80466-34-8; benzaldehyde, 100-52-7; 6-methyl-5-hepten-2-one, 110-93-0; phenylacetaldehyde, 122-78-1; citral, 5392-40-5; engenol, 97-53-0; β-ionone, 79-77-6.

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Received for review March 28, 1983. Revised manuscript received August 13, 1984. Accepted January 31, 1985. This research was funded in part by Sigma Xi Grant-in-Aid of Research and the Whitney Fund.