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Quality Parameters, Empirical and Kinetic Models of Lycopene and Beta-carotene Bioformation in Tomatoes (*Solanum lycopersicum*)

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This study examines a kinetic model estimating the geranyl geranyl pyrophosphate (GGPP) concentration in the carotenoid pathway in tomatoes (*Solanum lycopersicun*). Kinetics of bioformation of carotenoids in tomatoes of different cultivars (Cherry-Nasmata, VAR-10, and 4-lobes) at different ripening stages and conditions was used to evaluate the GGPP concentration in the kinetic model. Physicochemical parameters, lycopene and beta-carotene contents were assessed and compared under the two ripening conditions using standard laboratory procedures. The solid contents in the three cultivars of tomato were in the range of 5.61% to 6.85% and 5.83% to 7.16% at field and ambient temperature ripening, respectively; the pH values were all in the acidic region. Highest lycopene and beta-carotene concentrations were observed in 4-lobes cultivar at field ripening. The obtained data from the empirical and kinetic modeling showed the exponential models as first-order kinetics for both lycopene and beta-carotene bioformation in Cherry-Nasmata and 4-lobes cultivars. This suggests that beta-carotene bioformation depends on the pathway of lycopene in the tomato cultivars. The quality parameters of the tomato cultivars showed that ripening conditions influenced the quality of tomato contents. Also the GGPP concentrations of some of the tomatoes were successfully estimated using the kinetic model.

Keywords: Geranyl geranyl pyrophosphate, Lycopene, Beta-carotene, Kinetics, Empirical modeling

INTRODUCTION

Tomato is one of the most valuable and widely grown vegetable; each cultivar differs in fruit size, shape, taste, color, skin, and firmness of its flesh. Tomato is rich in organic acids, sugars, dietary fibre, pectic substances, proteins, and fats. It is also rich in minerals such as potassium, phosphorus, sulphur, magnesium, calcium, iron, copper, sodium, vitamins and carotenoids such as lycopene and β-carotene. The amount of carotenoids in tomato is determined by tomato cultivars and genotype [1]. The major goal of tomato breeders is obtaining cultivars with high market acceptability for using in both fresh and processed forms. Achieving the mentioned goal depends on the quality characteristics of tomatoes such as soluble solids, pH, total acidity, and color [2]. Tomatoes are also good sources of B-vitamins and vitamin K, α-tocopherol, and vitamin C. These vitamins are known for their potent antioxidant activities and are also involved in other physiological processes [3]. The main phytochemical in tomatoes is lycopene, which is a carotenoid pigment causing the red color of ripe tomatoes [4] and serving as an important antioxidant that counteracts the effect of harmful free radicals in human body. Many researchers have concluded that the antioxidant properties of lycopene are responsible for their ability to act against many diseases [5] including cancer. Tomatoes and tomato products provide about 85% of lycopene to human [6]. Lycopene is a factor antioxidant which is found predominately in all *trans* configuration. It is one of the predominant phytochemicals and an important

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bioactive compound in tomatoes [4]. Another important carotenoid is beta-carotene with orange pigment that is abundantly present in plants and fruits. It is regarded as one of the major carotenoid in human diet [7] and subsequently, the main source of vitamin A in humans. It is also a potent antioxidant that offers protection from age-related macular degeneration.

Carotenoid and other isoprenoid molecules are derived from Isopentenyl diphosphate (IPP) and its allylic isomer, dimethylallyl diphosphate (DMAPP) *via* cytosolic mevalonic acid (MVA) and plastidic methylerythritol 4-phosphate (MEP) pathways. Geranyl geranyl pyrophosphate (GGPP) is a immediate precursors of C-40 carotenoids, formed from IPP and DMAPP after a series of condensation reactions. In photosynthetic organisms, the rate-limiting reaction stage for carotenoid biosynthesis is the catalysis by the phytoene synthase enzyme [8]. The condensation of two molecules of GGPP by phytoene synthase (PSY) to form phytoene is the beginning of carotenoid biosynthesis. Phytoene is a colorless carotenoid formed by tail-to-tail condensation. Colored carotenoids are synthesized by phytoene desaturation reactions generating conjugated double bonds [9]. Four double bonds are introduced into phytoene *via* phytoene desaturase (PDS) and ζ-carotene desaturase (ZDS) enzymes forming tetra-cis-lycopene. Subsequently, isomerization of this compound via carotene isomerase (CRTISO) leads to the formation of all-trans lycopene [10,11]. It has been reported that CRTISO-like single-copy genes (CrtISO-L1 and CrtISO-L2) are present in tomato, Arabidopsis, and grape. The two enzymes were suggested to initiate a competing metabolic pathway metabolizing carotenes upstream of all-*trans*-lycopene [12]. The cyclization of lycopene by lycopene cyclase in carotenoid metabolism generates carotenoids with different cyclic-end groups. One branch of lycopene cyclization leads to β-carotene and its derivatives such as xanthophylls, while the other leads to α-carotene and subsequently, lutein. The biosynthetic pathway is a highly regulated process, however, the way the concentration of this precursor could be estimated in biological tissue has not been properly documented. Therefore, this work aimed to model the kinetic for estimating geranyl geranyl pyrophosphate (GGPP) concentration in the carotenoid pathway in tomatoes (*Solanum lycopersicun*).

EXPERIMENTAL

Seeds of three tomato cultivars (Cherry-Nasmata, Var-10, and 4-lobes) were obtained from the International Institute of Tropical Agriculture (IITA), Ibadan, Nigeria, and were planted on an organic farmyard at Kuye area, Ogbomoso, Nigeria. The tomatoes were harvested after three months of planting at different ripening stages, some of which were subjected to post-harvest ripening at ambient temperature, all with targeted ripening time. Total solid were analyzed by oven drying the tomato serum (5 g) at 105 °C for 3 h [13], the pH were determined in 30 g samples using a digital pH meter calibrated with buffer 4 and 7 [13]. The titratable acidity were done by titrating homogenized tomato samples with 0.01 M NaOH using phenolphthalein indicator [13]. The reducing sugar contents were carried out using antecedently described method [14]. Tomato serum (1 ml) was mixed with distilled water (99 ml), which corresponds to dilution factor of 100.1 ml of 5% phenol solution was added to 1 ml of the earlier prepared sample followed by addition of 5 ml concentrated H_2SO_4, the mixture was allowed to cool and the absorbance was taken (490 nm) using a UV-Vis spectrophotometer. The reducing sugar was estimated on the calibration curve using Beer-Lambert's law. The processes were carried out for each cultivar of tomatoes.

Extraction and Analysis of Carotenoids

The carotenoid contents (Lycopene and β-carotene) were determined using the previously employed solvent extraction method [15] considering some modifications. The extraction was carried out using 25 ml of 80% acetone and 20 ml n-hexane. The extract was treated with alcoholic KOH, methanol, and distilled water (1:1:1) to saponify the present triglycerides. It was later re-extracted with dilute n-hexane (dilution factor of 10); the extract was analyzed using Ultraviolet/Visible Spectrophotometer to determine the absorbance of lycopene and β-carotene at maximum wavelength of 450 and 502 nm, respectively. The concentrations of lycopene and β-carotene were simultaneously estimated as reported previously [16,17].

Data Analysis

All statistical analysis were performed using SPSS

software. Data were expressed as mean standard deviation and significance differences were determined by two-way Analysis of Variance (ANOVA) at $p < 0.05$ confidence interval. Experimental determination of each parameter was done in triplicates.

Kinetic Modeling

The kinetic was modeled using parallel and consecutive reactions, which explains the independency and dependency of beta-carotene on lycopene biosynthetic pathways, respectively.

Determination of the Maximum Ripening Times (t_{max}) of the Tomato Cultivars at Field and Ambient Temperature Ripening Conditions

The maximum ripening times (t_{max}) were calculated using the equation below:

$$t_{\max} = \frac{\ln\left(\frac{k_1}{k_2}\right)}{k_1 - k_2}$$

where k_1 and k_2 are first-order rate constants [18].

RESULTS AND DISCUSSION

Physico-chemical Parameters of the Three Cultivars of Tomatoes (Cherry-Nasmata, VAR-10 and 4-Lobes)

Table 1 presents the results for the variations in the physiological and biochemical properties of the three cultivars of tomato (Cherry-Nasmata, VAR-10 and 4-lobes) under field and ambient temperature ripening conditions. The total solid contents of Cherry-Nasmata, Var-10, and 4-lobes tomato cultivars varied from 5.61 to 6.85 % at field ripening, and from 5.83 to 7.16 % at ambient temperature ripening. The solid contents in Cherry-Nasmata and VAR-10 cultivars were higher (6.85 and 6.20 %) at field ripening than the values obtained at ambient temperature ripening (5.83 and 6.0%). However, highest value of 7.16% was obtained for 4-lobes cultivar of tomato at ambient temperature, and 5.61% for self-ripened tomatoes. This suggests that 4-lobes tomato cultivar under ambient temperature ripening condition have higher contents of organic compound, mineral, and crude fiber. The observed changes in total solid contents of the three cultivars of tomatoes were in agreement with previous reports that in

Table 1. Physico-chemical Properties of Cherry-Nasmata, VAR-10 and 4 Lobes Cultivars of Tomatoes at Field and Ambient Temperature Ripening Conditions

Quality parameter	Tomato cultivar		
	Field ripening		
	Cherry-Nasmata	VAR-10	4-Lobes
Total solids (%)	6.85 ± 0.20^a	6.20 ± 0.18^a	5.61 ± 0.17^a
pH	3.89 ± 0.12^a	3.81 ± 0.11^b	3.80 ± 0.11^c
Titratable acidity (%)	0.32 ± 0.02^a	0.20 ± 0.01^a	0.18 ± 0.01^b
Reducing Sugar (g/100 g)	2.63 ± 0.11^a	4.65 ± 0.01^a	2.95 ± 0.04^a
Lycopene (μg g^{-1})	18.69 ± 1.1^a	13.19 ± 0.96^a	28.03 ± 2.53^a
Beta-carotene (μg g^{-1})	4.67 ± 0.35^a	3.30 ± 0.29^a	7.01 ± 0.60^a
	Ambient temperature ripening		
	5.83 ± 0.17^b	6.00 ± 0.18^a	7.16 ± 0.21^a
	5.35 ± 0.16^a	4.01 ± 0.12^a	3.74 ± 0.11^b
Total solids (%)	0.20 ± 0.01^b	0.19 ± 0.01^a	0.26 ± 0.01^a
pH	2.52 ± 0.08^a	3.51 ± 0.15^a	2.93 ± 0.03^a
Lycopene (μg g^{-1})	12.38 ± 1.11^b	10.40 ± 1.29^a	18.9 ± 2.05^a
Beta-carotene (μg g^{-1})	3.10 ± 0.17^b	2.60 ± 0.12^a	4.74 ± 0.39^a

which tomatoes were composed of 93-95% water, while other constituents including inorganic compounds, organic acids (citric and malic), sugars (glucose, fructose, and sucrose), insoluble solids in alcohol (proteins, cellulose, pectin, and polysaccharides), carotenoids, and lipids were 5-7% [2]. The solid content in Cherry-Nasmata and VAR-10 cultivars of tomato at field and ambient temperature ripening were also in line with a previous study on the same tomato cultivars (Cherry-Nasmata and VAR-10), and other cultivars (Ajindi-Kerewa and Beske) [19,20].

The pH values at ambient temperature for studied Cherry-Nasmata and VAR-10 cultivars of tomato were 5.35 and 4.01, respectively. The corresponding values at field ripening conditions were 3.89 and 3.81 for Cherry-Nasmata and VAR-10, respectively. The 4-lobes tomato cultivar had pH value of 3.80 at field ripening and 3.74 at ambient temperature ripening. This implies that the Cherry-Nasmata (3.89) and VAR-10 tomato cultivars (3.81) ripened at the field temperature, and the 4-lobes cultivar ripened at ambient temperature are more acidic and may taste sour; higher pH value implies low acidity and a better taste. The most important prevailing factors for tomato flavor are sugar and acid contents. The acid contents of fruits change as a result of reduction in malic and citric acid contents of the flesh [21]. Acidity has a greater influence on the taste and shelf-life of tomatoes by preventing microbial spoilage. The titratable acidity values of the three cultivars of tomatoes also vary with the ripening conditions (Table 1); this is in agreement with the previous report on the percentage of titratable acidity with Beske cultivar under field ripening, and Ajindi-Kerewa at ambient temperature ripening [20].

Based on the results obtained from this study, the reducing sugar contents were higher in all the cultivars at field ripening than ambient temperature ripening (Table 1). Among the cultivars under study, 4-lobes cultivar obeys the pH and sugar content relationship in both field and ambient temperature ripening conditions, which implies that a tomato with low sugar and high acid contents tend to be sour, and sweet tomatoes have high sugar and low acid contents. However, observed disparity in the pH/sugar content relationship in other cultivars (Cherry-Nasmata and VAR-10) at both ripening conditions may be due to the nature of these cultivars and/or other factors such as genotype [1].

Lycopene and beta-carotene contents of the three cultivars of tomato varied with ripening conditions (Table 1). One of the predominant phytochemicals and an important bioactive compound in tomatoes is lycopene [4]. The lycopene contents in all the studied tomato cultivars were higher at field temperature ripening compared to those at ambient temperature ripening. The lycopene contents in Cherry-Nasmata and VAR-10 cultivars were 18.69 μg g^{-1} and 13.19 μg g^{-1} at field ripening which is higher than the values obtained at ambient temperature ripening, 12.38 μg g^{-1} and 10.40 μg g^{-1} for the two cultivars, respectively. Highest lycopene concentration was observed in 4-lobes cultivar; which was 28.03 μg g^{-1} at the field ripening, and 18.90 μg g^{-1} at the ambient temperature ripening.

Beta-carotene is a precursor to vitamin A due to its ability to yield two molecules of retinol in the presence of oxygen, a reaction that is catalyzed by β-carotene 15,15′-monooxygenase. It is generated from the biosynthesis and cyclization of lycopene. The results showed the same trend as the results for lycopene: highest beta-carotene content was found in 4-lobes cultivar (7.01 μg g^{-1} and 4.74 μg g^{-1}) followed by Cherry-Nasmata (4.67 μg g^{-1} and 3.10 μg g^{-1}) and VAR-10 (3.30 μg g^{-1} and 2.60 μg g^{-1}) at field and ambient temperature ripening conditions respectively.

However, the significant differences of the physico-chemical parameters were obtained. The mean values for the three tomato cultivars were significantly different at $p \leq 0.05$ level for the total solid contents, titratable acidity, sugar contents, lycopene, and beta-carotene. The mean values for the pH were not significantly different at the $p \leq 0.05$ level at field ripening.

Values are mean of three replicates ± standard deviation; values with the same alphabets along the rows are significantly different at $p \leq 0.05$ while those with different alphabets are not significantly different at the same confidence interval at each ripening conditions.

Variation of Lycopene and β-carotene Concentrations with Ripening Time in the Three Cultivars of Tomato

The increase in lycopene concentrations with respect to

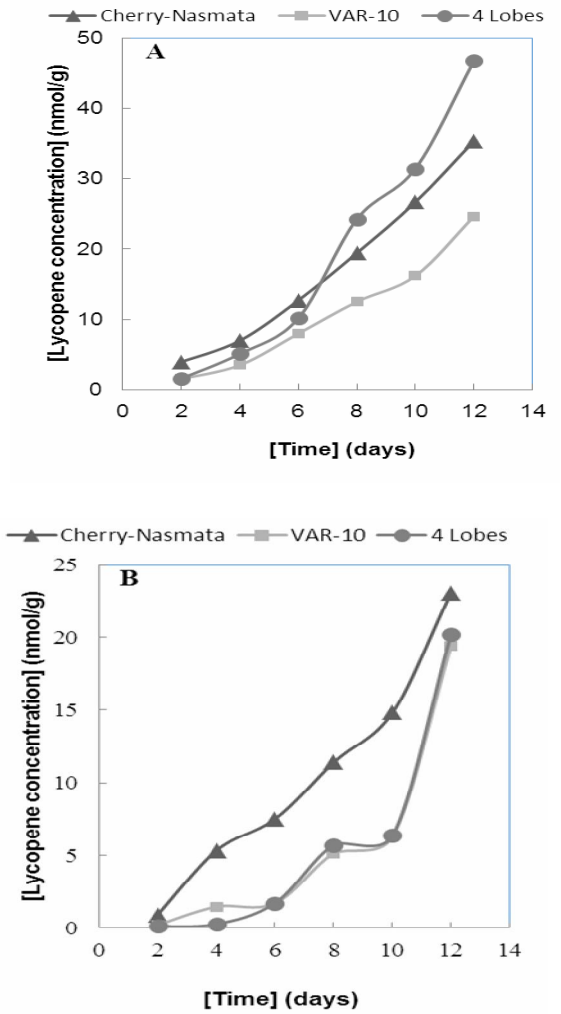

Fig. 1. Time variation of lycopene concentrations in Cherry-Nasmata, Var-10, and 4-lobes tomato cultivars under (A) field ripening and (B) ambient temperature ripening.

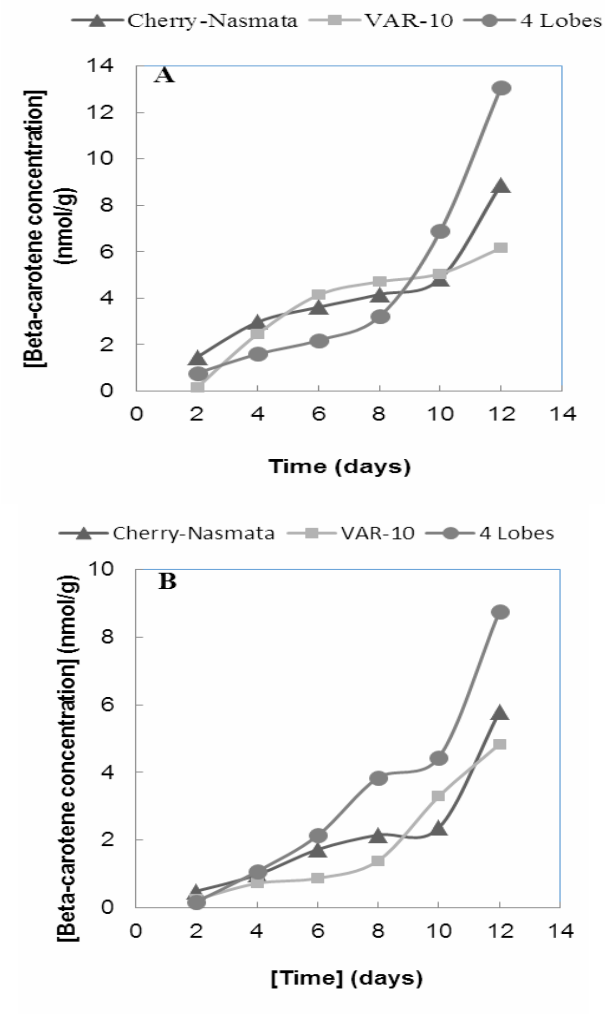

Fig. 2. Time variation of β-carotene concentrations in Cherry-Nasmata, Var-10, and 4-lobes tomatoes cultivars under (A) field ripening and (B) ambient temperature ripening.

time for the three cultivars of tomato (Cherry-Nasmata, VAR-10, and 4-lobes) under field and ambient ripening conditions are shown in Figs. 1A and 1B, respectively. Maximum concentrations of lycopene content (46.70, 35.33, and 24.61 nmol g^{-1} for 4-lobes, Cherry-Nasmata, and Var-10 cultivars, respectively) were observed on the 12th day when the tomatoes were at fully red ripening stage under field ripening condition; this is in agreement with the previous report that showed the optimal concentration of lycopene obtained at fully ripening stage under field ripening [22]. Maximum lycopene concentrations on the 12th day of the bioaccumulation process under ambient temperature ripening condition were 23.09, 20.21, and 19.40 nmol g^{-1} for Cherry Nasmata, 4-Lobes, and VAR-10, respectively.

Similarly, the variation of the β-carotene contents in the three cultivars of tomatoes at field and ambient temperature ripening conditions are shown in Figs. 2A and 2B, respectively. According to the results, the bioformation of β-carotene increases gradually with increasing ripening

time. Beta-carotene bioformation were all higher for field-ripened tomatoes than those subjected to ambient temperature ripening condition, this is similar to the results that has been reported earlier [20]. However, the highest β-carotene concentration of 13.07 nmol g^{-1} and 8.77 nmol g^{-1} were found in 4-Lobes cultivar at field ripening and ambient temperature ripening conditions, respectively.

Empirical Models for Lycopene and Beta-carotene Bioaccumulation for the Three Cultivars of Tomatoes

The lycopene bioaccumulation in the three cultivars of tomatoes under field and ambient temperature ripening conditions were subjected to both linear and exponential empirical models as shown in Table 2. Considering linear empirical model, correlation coefficient (R^2) values of 0.979, 0.964, and 0.954 were obtained for Cherry-Nasmata, VAR-10, and 4-Lobe, respectively. However, the R^2 values obtained from the exponential empirical model at field ripening condition were 0.976, 0.954, and 0.950, respectively. This shows that the linear and exponential empirical models show the best fit for the bioaccumulation of lycopene content in the studied cultivars under field ripening conditions. However, at ambient temperature ripening, only Cherry-Nasmata cultivar best described the linear empirical model with R^2 value of 0.959. In contrast to Cherry-Nasmata, both VAR-10 and 4-Lobes were best described by an exponential empirical model with R^2 values of 0.931 and 0.956, respectively.

The empirical model for the bioformation of beta-carotene is shown in Table 3. The obtained R^2 values show that VAR-10 is best described by the linear model (R^2 = 0.907), and the both Cherry-Nasmata and 4-Lobes are best described by the exponential empirical model (R^2 = 0.914 and 0.982) at field ripening condition. The trend observed under ambient ripening condition indicates that the linear empirical model best described the bioformation of beta-carotene in only 4-Lobes cultivar (R^2 = 0.909). For Cherry-Nasmata and VAR-10, the best fit obtained using exponential empirical model with R^2 values of 0.940 and 0.967, respectively. Moreover, the linear and exponential models are related to zero and first-order kinetics, respectively. This suggests that lycopene bioformation could possess either first or zero-order kinetics.

Table 2. Empirical Models for Lycopene Bioaccumulation in the Three Cultivars of Tomatoes at Field and Ambient Temperature Ripening Conditions

Field ripening					
Function	Modelequations	Model parameters	Tomato cultivars		
			Cherry-nasmata	VAR-10	4-Lobes
		A	3.180	2.255	4.551
Linear	At + B	B	-4.757	-4.743	-11.99
		R^2	0.979	0.964	0.954
		E	2.924	1.170	1.176
Exponential	$L = Ee^{-Ft}$	F	0.219	0.269	0.331
		R^2	0.976	0.954	0.950
Ambient temperature ripening					
		A	2.045	1.625	1.760
Linear	At + B	B	-3.809	-5.669	-6.61
		R^2	0.959	0.733	0.752
		E	1.021	0.162	0.052
Exponential	$L = Ee^{-Ft}$	F	0.279	0.398	0.511
		R^2	0.855	0.931	0.956

Table 3. Empirical Models for Beta-carotene Bioaccumulation in the Three Cultivars of Tomatoes at Field and Ambient Temperature Ripening Conditions

Field ripening					
Function	Model equations	Model parameters	Tomato cultivars		
			Cherry-Nasmata	VAR-10	4-Lobes
		A	0.617	0.547	1.119
Linear	At + B	B	0.000	- 0.051	- 3.213
		R^2	0.844	0.907	0.809
		E	1.30	0.314	0.459
Exponential	$L = Ee^{-Ft}$	F	0.151	0.295	0.269
		R^2	0.914	0.630	0.982
Ambient temperature ripening					
		A	0.444	0.446	0.795
Linear	At + B	B	- 0.863	- 1.227	- 2.188
		R^2	0.786	0.868	0.909
		E	0.371	0.166	0.175
Exponential	$L = Ee^{-Ft}$	F	0.217	0.285	0.346
		R^2	0.940	0.967	0.892

Table 4. Kinetic Data for Lycopene and Beta-carotene Bioformation in Cherry-Nasmata, VAR-10 and 4-Lobes Cultivars of Tomatoes

		Field ripening condition				Ambient temperature ripening condition			
		Zero-order		First-order		Zero-order		First-order	
Carotenoids	Cultivars	Rate constant (nmol g^{-1} day^{-1})	RR^2	Rate constant (day^{-1})	RR^2	Rate constant (nmol g^{-1} day^{-1})	RR^2	Rate constant (day^{-1})	RR^2
Lycopene	Cherry-Nasmata	2.818	0.915	0.158	0.938	1.606	0.904	0.119	0.973
	VAR-10	1.884	0.931	0.127	0.970	0.971	0.586	0.049	0.912
	4-Lobes	3.727	0.828	0.141	0.957	0.998	0.576	0.053	0.887
Beta-Carotene	Cherry-Nasmata	0.617	0.844	0.071	0.979	0.345	0.737	0.057	0.978
	VAR-10	0.541	0.907	0.215	0.976	0.304	0.760	0.118	0.722
	4-Lobes	0.748	0.699	0.076	0.778	0.543	0.798	0.091	0.972

Kinetics of Lycopene and Beta-carotene Bioformation in the Three Cultivars of Tomatoes

Table 4 shows the obtained kinetic parameter as well as the correlation coefficient (R^2) for all the cultivars of tomato under field and ambient temperature ripening conditions. It was shown that the rate of bioformation of lycopene at field

ripening condition can best be described using both zero-order and first-order kinetic models. The Cherry-Nasmata cultivar had the highest rate of lycopene bioaccumulation with rate constant of 2.818 nmol g^{-1} day^{-1} and R^2 value of 0.915, and rate constant of 0.158 $days^{-1}$ with R^2 value of 0.938 for the zero and first order kinetics, respectively. This is in agreement with the empirical modeling of the parameters for the tomato cultivars described above. Similarly, the bioformation of beta-carotene under the same ripening condition showed that VAR-10 cultivar had the fastest rate of bioaccumulation of beta-carotene for the zero-order kinetic model (rate constant of 0.541 nmol g^{-1} day^{-1} and R^2 value of 0.907) and the first-order kinetic model (rate constant of 0.215 $days^{-1}$ and R^2 value of 0.976). On the other hand, the kinetic model for the bioformation of lycopene under ambient temperature ripening condition suggests the both zero-order kinetic model (rate constant of 0.606 nmol g^{-1} day^{-1} and R^2 value of 0.904) and first-order kinetic model (rate constant of 0.119 day^{-1} and R^2 value of 0.973) to describe the bioformation of lycopene in Cherry Nasmata, whereas for VAR-10 and 4-Lobe, the best results obtained using only first-order kinetic model. The trend of the bioformation of beta carotene under ambient temperature ripening condition indicates that first-order kinetic model best describes the process. However, a study [19] has previously reported a first-order kinetic model for lycopene bioformation at ambient temperature ripening condition for Ajindi-Kerewa, Beske, 3-Lobes, and Big Local cultivars of tomatoes.

Kinetic Modeling

The kinetic was modeled using parallel and consecutive reactions representing cases I and II, respectively.

Case I: This is based on the assumption that lycopene and beta-carotene bioformations are dependent on geranyl geranyl pyrophosphate concentration, and beta-carotene is independent of lycopene biosynthetic pathway. This assumption is based on the following equations:

$$2G \xrightarrow{k_1} L \quad (1)$$

$$2G \xrightarrow{k_2} B \quad (2)$$

where G, L, and B represent geranyl geranyl pyrophosphate, lycopene, and beta-carotene, respectively, and k_1 and k_2 are the first order rate constants for the carotenoids. In a case whereby the bioformation of both lycopene and beta-carotene follow the first order kinetics, the following equations are used:

The rate equations for [G], [L], and [B];

$$\frac{d[G]}{dt} = -2k_1[G] - 2k_2[G] \quad (3)$$

$$\frac{d[L]}{dt} = 2k_1[G] \quad (4)$$

$$\frac{d[B]}{dt} = 2k_2[G] \quad (5)$$

From (3); $\frac{d[G]}{dt} = -2k_1[G] - 2k_2[G]$

$$\frac{d[G]}{dt} = -2(k_1 + k_2)[G] \quad (6)$$

$$\int_{G_0}^{G} \frac{d[G]}{[G]} = -2(k_1 + k_2)\int_0^t dt \quad (7)$$

$$\ln\left(\frac{[G]}{[G]_0}\right) = -2(k_1 + k_2)t \quad (8)$$

$$[G] = [G]_0 \exp^{-2(k_1 + k_2)t} \quad (9)$$

$$\int d[L] = 2k_1[G]_0 \int \exp^{-2(k_1 + k_2)t} dt \quad (10)$$

$$[L] = \frac{2k_1}{2(k_2 - k_1)}[G]_0 \exp^{-2(k_1 + k_2)t} \quad (11)$$

$$[L] = \frac{k_1}{(k_2 - k_1)}[G]_0 \exp^{-2(k_1 + k_2)t} \quad (12)$$

If $k_1 >> k_2$ then $\exp^{-2k_1t} << \exp^{-2k_2t}$

$$[L] = [G]_0 \exp^{-2k_2t} \quad (13)$$

If $k_2 >> k_1$ then $\exp^{-2k_2t} << \exp^{-2k_1t}$

$$[L] = \frac{k_1}{k_2}[G]_0 \exp^{-2k_1t} \quad (14)$$

From Eq. (5), $\frac{d[B]}{dt} = 2k_2[G]$

$$[B] = \frac{k_2}{(k_2 - k_1)}[G]_0 \exp^{-2(k_1 + k_2)t}$$

$$[B] = \frac{k_2}{(k_2 - k_1)} \quad (15)$$

Case II: This is based on the assumption that lycopene bioformation is dependent on geranyl geranyl pyrophosphate, and beta-carotene is formed from lycopene cyclization. This assumption is based on the following equation:

$$2G \xrightarrow{k_1} L \xrightarrow{k_2} B \quad (16)$$

Where G, L, and B represent the concentrations of geranyl geranyl pyrophosphate, lycopene, and beta-carotene, respectively, and k_1 and k_2 are the first order rate constants for the carotenoids. In the case whereby the bioformation of both lycopene and beta-carotene follow the first order kinetics, the following equations are used:

The rate equations for [G], [L] and [B] are:

$$\frac{d[G]}{dt} = -2k_1[G] \quad (17)$$

$$\frac{d[L]}{dt} = 2k_1[G] - k_2[L] \quad (18)$$

$$\frac{d[B]}{dt} = k_2[L] \quad (19)$$

From Eq. (17), $\int_{G_0}^{G} \frac{d[G]}{[G]} = -2k_1 \int_0^t dt \quad (20)$

$$\ln\left(\frac{[G]}{[G_0]}\right) = -2k_1 t \quad (21)$$

$$[G] = [G]_0 \exp^{-2k_1 t} \quad (22)$$

From (18), $\frac{d[L]}{dt} = 2k_1[G] - k_2[L] \quad (23)$

$$\frac{d[L]}{dt} + k_2[L] = 2k_1[G] \quad (24)$$

$$[L] = \frac{2k_1}{k_2 - 2k_1}[G]_0(\exp^{-2k_1 t} - \exp^{-k_2 t}) \quad (25)$$

If $k_1 >> k_2$ then $\exp^{-2k_1 t} << \exp^{-2k_2 t}$

$[G] = [G]_0$, $[L] = 0$, $[B] = 0$

By mass conservation,

$$[G]_0 = [G] + [L] + [B] \quad (26)$$

Where $[A]_0$ is the initial concentration at time t = 0

$$[C] = [G]_0 - [G] - [L] \text{ by mass conservation,} \quad (27)$$

Substituting the values of [G] and [L] into Eq. (27)

$$[B] = [G]_0 - [G]_0 \exp^{-2k_1 t} - \frac{2k_1}{k_2 - 2k_1}[G]_0(\exp^{-2k_1 t} - \exp^{-k_2 t}) \quad (28)$$

$$[B] = [G]_0\left[1 - \exp^{-2k_1 t} - \frac{2k_1}{k_2 - 2k_1}\left(\exp^{-2k_1 t} - \exp^{-k_2 t}\right)\right] \quad (29)$$

$$[B] = [G]_0\left[1 - \frac{2k_1}{k_2 - 2k_1}\left(\exp^{-2k_1 t} - \exp^{-k_2 t}\right) - \exp^{-2k_1 t}\right] \quad (30)$$

In the two predicted cases for estimating the G_o values (total geranyl geranyl pyrophosphate) for the three cultivars of tomatoes, positive G_o values were obtained for Cherry-Nasmata and 4-Lobes tomato cultivars at field and ambient temperature ripening under cases I and II conditions. A negative G_o value at ambient temperature ripening was obtained for 4-lobes tomato cultivar under case I conditions. However, estimating the G_o values failed for VAR-10 tomato cultivar in both cases except at ambient temperature ripening under case II (Table 5). It is suggested that cases I and II can be used for estimating the concentration of GGPP in the carotenoid pathway of fruits, though, the method for estimating the G_o concentration in the carotenoid pathway is more of biological process.

The maximum ripening time (t_{max}) of the three tomato cultivars were derived. It was found that t_{max} vary with ripening conditions. It ranges from 6 to 9 days at field

Table 5. Estimation of GGPP Concentrations in the Three Cultivars of Tomato

Tomato cultivars	Total geranyl geranyl pyrophosphate (GGPP) concentration (nmol g^{-1})			
	Field ripening		Ambient temperature ripening	
	Case I	Case II	Case I	Case II
Cherry-Nasmata	33.85	12.85	18.54	45.89
VAR-10	-39.09	-93.44	-33.37	53.40
4-Lobes	18.04	30.38	-17.92	0.000391

Table 6. Estimated Maximum Ripening Time (t_{max}) of the tomato Cultivars at Field and Ambient Ripening Conditions

Tomato cultivars	t_{max} (days)	t_{max} (days)
	(Field ripening)	(Ambient temperature ripening)
Cherry-Nasmata	9	12
VAR-10	6	13
4-Lobes	10	14

ripening and from 12 to 14 days at ambient temperature ripening. The ripening time is longer (14 days) in tomatoes that were subjected to ambient temperature ripening conditions compared to self-ripened tomatoes (Table 6). This implies that ambient temperature ripened tomatoes have longer times of ripening and longer shelf life compared to self-ripened tomatoes.

CONCLUSIONS

Nutritional and phytochemical importance of lycopene and beta-carotene in preventing and combating cardiovascular diseases has been the attractive subject of research on the phytonutrients. Current investigation on the kinetics of bioaccumulation of lycopene and beta-carotene in three cultivars of tomatoes at field and ambient temperature ripening conditions suggest that VAR-10 cultivar of tomato has the least concentration of lycopene and beta-carotene under the both ripening conditions. 4-Lobes cultivar had the highest accumulated beta-carotene concentration under field and ambient temperature ripening conditions; it also has the highest accumulated lycopene under field ripening condition. These variations may be due to some factors including genotype. There was a convincing agreement between the empirical modeling and the kinetic modeling: the bioaccumulation of lycopene concentration under field ripening condition can best be described using both zero-order and first-order kinetic models.

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