CHANGES IN SUGAR AND ACID COMPOSITION OF 'AMBRA' NECTARINES DURING SHELF LIFE BASED ON NON-DESTRUCTIVE ASSESSMENT OF MATURITY BY TIME-RESOLVED REFLECTANCE SPECTROSCOPY

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A B S T R A C T

One of the non-destructive techniques which have been developed to estimate fruit quality is time-resolved reflectance spectroscopy (TRS). TRS measures the absorption (μ_a) and scattering (μ_s') of pulses of laser light passing through the fruit. The absorption coefficient at 670 nm coincides with the absorption peak of chlorophyll, and has been used to estimate maturity of nectarines at harvest and to predict their softening rate during shelf life. A relatively low μ_a at 670 nm indicates that the fruit is more mature and that it will soften earlier, whereas a relatively high μ_a at 670 nm indicates that the fruit is less mature and that it will soften later. The aim of this research was to study the relationships between maturity of nectarines at harvest time as measured by TRS and its sugar and organic acid composition during shelf life. Nectarines of the cultivar 'Ambra' were harvested on the second commercial picking date (July 5, 2004). The fruit were sorted by size and were measured for their absorption coefficient (μ_a) using TRS at 670 nm. Fruit of each maturity class were randomized among the different samplings, so that the fruit from whole range of μ_a was represented in each sample. Total soluble solids (TSS), titratable acidity (TA), sugars and organic acids were measured at harvest time and at various times during

shelf life at 20°C. Data were statistically elaborated using step-wise multiple linear regression analysis. μ_a had significant effect on the sugar and acid contents of fruit. As the fruit matured on the tree, total soluble solids, total sugars, the proportion of sucrose, the proportion of malic acid and the proportion of quinic acid increased. On the other hand, the proportion of fructose, the proportion of sorbitol, total acids and especially the proportion of citric acid decreased. During shelf life at 20°C, total acids decreased, and sugars were less affected. Therefore, individual fruits can be sorted according to fruit quality by using TRS to measure μ_a at harvest time.

Keywords: *Prunus persica* [L.] Batsch, nectarines, maturity, non-destructive technology, time-resolved reflectance spectroscopy, soluble solids, sugars, acids

INTRODUCTION

Peaches and nectarines (*Prunus persica* [L.] Batsch) are valued for their characteristic flavour and taste. Because the fruits do not uniformly mature on the tree at the same time, they have to be harvested in several batches according to various maturity indices. A good harvesting index for peaches and nectarines is the background skin colour, which turns from green to yellow as chlorophyll content decreases (Delwiche and Baumgardner, 1985; Eccher Zerbini et al., 1994).

However, many of the newer cultivars have a red blush, which masks the background colour, making it virtually impossible to visually determine the maturity stage. In peaches and nectarines, maturity is said to be the stage when fruit reaches a sufficient development while on tree. On the other hand, ripening of peaches and nectarines are specifically storage associated changes that transform a mature fruit into one ready to eat (Crisosto, 1994). Hence, maturity at harvest determines the quality of fruit when it reaches the consumer.

When the harvest date is postponed, fruit mass increases by two to ten grams a day. There is also an increase in sugar and flavour components (Bassi et al., 1995; Rizzolo et al., 1993; Vanoli et al., 1993; Haji et al., 2004). As the fruit mature on the tree, glucose and fructose are converted into sucrose, the predominant sugar in the ripe fruit (Kobashi et al., 1999; Moriguchi et al., 1990). There is also an increase in malic acid and a decrease in citric acid (Meredith et al., 1989; Vanoli et al., 1993).

Many non-destructive techniques have been developed in order to ensure maximum fruit quality. Time-resolved reflectance spectroscopy (TRS) has been used to estimate the maturity of nectarines at the time of harvest and to predict their softening rate during shelf life. TRS measures the absorption (μ_a) and scattering coefficient (μ_s') of pulses of laser light passing through the fruit. The absorption coefficient at 670 nm relates to the absorption peak of chlorophyll and can be used to estimate maturity in nectarines. A relatively low μ_a at 670 nm indicates that the fruit is more mature and that it will soften earlier, whereas a relatively high μ_a at 670 nm indicates that the fruit is less mature and that it will soften later (Eccher Zerbini et al., 2003, 2005, and 2006). The aim of this research was to study the relationships between the maturity of nectarines at harvest as measured by TRS and their sugar and organic acid composition during shelf life.

MATERIAL AND METHODS

In 2004, nectarines of the cultivar 'Ambra' were harvested on the second commercial picking date (July 5). The nectarines were collected from a commercial orchard in Faenza, near Ravenna, Italy.
After picking, the fruits were sorted into two size classes:

- Larger (size A): 73.0 to 79.9 mm in diameter; and
- Smaller (size B): 67.0 to 72.9 mm in diameter.

At harvest, 180 fruits of each size were individually weighed and measured using TRS at 670 nm. The absorption coefficients were ranked, and the fruits were divided into three maturity classes: high, medium and low. Fruits in each maturity class were randomized among the different samplings, so that fruit from whole range of μ_a was represented in each sample.

Fruit were analyzed after 20, 26, 45, 69, 93 and 117 hours at 20°C. At each time of analysis, two replicates of five fruits per size and maturity class were used; the fruits from each replicate were sliced, pooled, immediately deep frozen, and kept at -20°C until analysis. The data recorded at each time of analysis included total soluble solids (TSS), titratable acidity (TA), sugars, and organic acids.

Sucrose, glucose, fructose, sorbitol, quinic acid, malic acid and citric acid were measured using HPLC (Forni et al., 1992 and Vanoli et al., 1993). Data were recorded as g/100 g fresh weight. Total sugars and total acids were computed as the sums of the individual sugars and acids. The proportions of each individual sugar or acid to the total sugars or acids were also calculated.

Data were statistically elaborated using multiple linear regression analysis (PROC REG, SAS/STAT, SAS Institute Inc., Cary, NC, 2004). While running PROC REG, an automatic step-wise procedure was used.

In addition to the automatic procedure, some alternative models were evaluated by changing the set of variables in the model. The models were selected according to two criteria: higher R^2 and simplicity. Only variables significant at $P < 0.05$ were included in the final equations.

First, because all dependent variables in our model equation suggested a linear trend, Equation 1 was used to study the effect of μ_a, fruit mass (m_{fruit}) and time (t) on TSS, TA, total sugars, individual sugars, total acids and individual acids:

$$y = a + b_1 x_1 + b_2 x_2 + b_3 x_3 + b_{12} x_1 x_2 + b_{13} x_1 x_3 + b_{23} x_2 x_3 \qquad (1)$$

where y is the dependent variable (sugar or acid content); x_1, x_2, x_3 are the independent variables (μ_a, fruit mass and time, respectively), x_1x_2, x_1x_3 and x_2x_3, are the interactions between independent variables, the parameters b_i are the coefficients of the independent variables, and a is the intercept.

However, when the results were more closely examined, total acids and the proportion of sorbitol followed a logarithmic trend as a function of time as described in Equation 2:

$$y = a + b_1x_1 + b_2x_2 + b_3(\log_e x_3) + b_{12}x_1x_2 + b_{13}x_1(\log_e x_3) + b_{23}x_2(\log_e x_3) \quad (2)$$

The proportion of citric acid showed a non-linear progression, with a steep rise up to a value of μ_a of 0.12 cm^{-1}, at which point it levelled off. Mathematically, either a second degree polynomial equation or a logistic equation could fit the data observed.

With the second degree polynomial equation, the proportion of citric acid would decrease at higher values of μ_a characteristic for immature fruits. With the logistic equation, the proportion of citric acid would become asymptotic at higher values of μ_a. On the other hand, the proportion of citric acid would decrease more steeply at lower levels of μ_a with the polynomial model, but less and less steep with the logistic model. From a physiological point of view, the logistic model seemed to be more reasonable, at least for the values of μ_a observed. The logistic model also had a higher R^2. Therefore, Equation 3 was used to describe trends in the proportion of citric acid:

$$Cit = \frac{Cit_{max}}{1 + e^{b_m \cdot \mu_a + c}} \quad (3)$$

where Cit is the proportion of citric acid, Cit_{max} is its maximum level, b_m is the coefficient of μ_a and c is the constant.

Because Equation 3 is non-linear, the data for citric acid were elaborated using non-linear regression (PROC NLIN, SAS/STAT, SAS Institute Inc., Cary, NC, 2004).

RESULTS

Average fruit mass was 166 grams for the larger size class and 134 grams for the smaller size class. There was a negative correlation between fruit mass and μ_a (r = −0.46). The higher the fruit mass, the lower the μ_a and consequently, the more mature the fruit.

There was a very strong positive correlation between TA and total acids (r = 0.85). There was also a very strong positive correlation between TSS and total sugars (r = 0.73). The results for regression analysis are presented in Table 1.

The coefficients of determination (R^2) were not very high, and were lower for sugars than for acids. This indicates that a large amount of variability could not be explained by the independent variables.

TSS, total sugars and the proportion of sucrose increased as μ_a decreased, that is, as the fruit matured. On the other hand, the proportion of fructose and the proportion of sorbitol decreased (Fig. 1 c and g). The proportion of glucose did not change with μ_a.

TSS, total sugars, the proportion of sucrose and the proportion of sorbitol increased with increasing fruit mass, whereas the proportion of glucose and the proportion of fructose decreased (Tab. 1).

The interaction of fruit mass and μ_a was statistically significant with TSS, total sugars, and the proportion of sorbitol, all of which increased with increasing mass. However, this increase was higher at lower values for μ_a for TSS and total sugars, and at higher values of μ_a for sorbitol.

Sugar composition changed slightly during shelf life. The proportions of glucose and fructose increased, while the proportions of sucrose and sorbitol decreased (Fig. 1). There was no significant change in TSS and total sugars.

On the other hand, there was a significant decrease in TA and total acids during shelf life, mainly because of a decrease in both citric and malic acids (data not shown). The proportion of malic acid decreased while the proportion of quinic acid increased (Fig. 2).

The increase in the proportion of quinic acid during shelf life was higher at lower values of μ_a, that is, in mature fruit.

The proportion of citric acid did not change much as a function of time, rather than as a function of μ_a. The proportion of citric acid decreased markedly at values of μ_a less than 0.12 cm^{-1}, that is, in mature fruit (Fig. 2g).

Total acids decreased with decreasing μ_a, whereas the proportions of malic and quinic acids increased.

In less mature fruit with a higher μ_a, total acids increased and the proportion of quinic acid decreased with increasing fruit mass. The proportion of malic acid increased with increasing fruit mass only in mature fruit with lower values for μ_a.

DISCUSSION

With TRS, individual fruits can be sorted for fruit quality on the basis of sugar and acid composition. Furthermore, measuring μ_a at 670 nm separates the effects due to maturation on the tree from the effects due to ripening during shelf life at 20°C.

Both fruit mass and μ_a were measured at harvest. Any differences in μ_a among individual fruits at harvest time were due to the process of maturation on the tree. Therefore, any differences in sugars or acids that are related to μ_a are due to pre-harvest factors. The same holds true for the fruit mass.

T a b l e 1 . Parameters estimated by regression (see equation 1, 2 and 3) and R^2 of selected models for sugar and acid variation in function of absorption coefficient at 670 nm (μ_a), fruit mass (m_{fruit}), time at 20°C (t) and their interactions. Variables with non significant coefficient (such as $m_{fruit} \times t$) were excluded from the model. All the regressions and all the parameters included in the equation are significant at level <0.05

Dependent Variables	Coefficients of independent variables							Constant	R^2
	μ_a [cm^{-1}]	t [h]	m_{fruit} [g]	$Log_e t$	$\mu_a \times m_{fruit}$	$\mu_a \times t$	Cit_{max}		
TSS [°Brix]	-	-	0.017	-	-0.074	-	-	8.5	0.45
Total Sugars [g/100 g FW]	-	-	0.026	-	-0.047	-	-	4.2	0.51
Sucrose [%]	-15.1	-0.017	0.049	-	-	-	-	70	0.47
Glucose [%]	-	0.006	-0.025	-	-	-	-	12.9	0.33
Fructose [%]	7.85	0.016	-0.029	-	-	-	-	16.4	0.55
Sorbitol [%]	-	-	-	-0.260	0.020	-	-	2.5	0.56
TA [meq/100 g FW]	-	-0.034	-	-	0.22	-	-	16.4	0.70
Total Acids [g/100 g FW]	-	-	0.001	-0.149	0.019	-	-	1.4	0.78
Quinic [%]	-	0.064	-	-	-0.118	0.28	-	15.3	0.71
Malic [%]	-	-0.024	0.096	-	-0.764	-	-	40.2	0.66
Citric [%]	-32.3	-		-	-	-	49	1.14	0.74

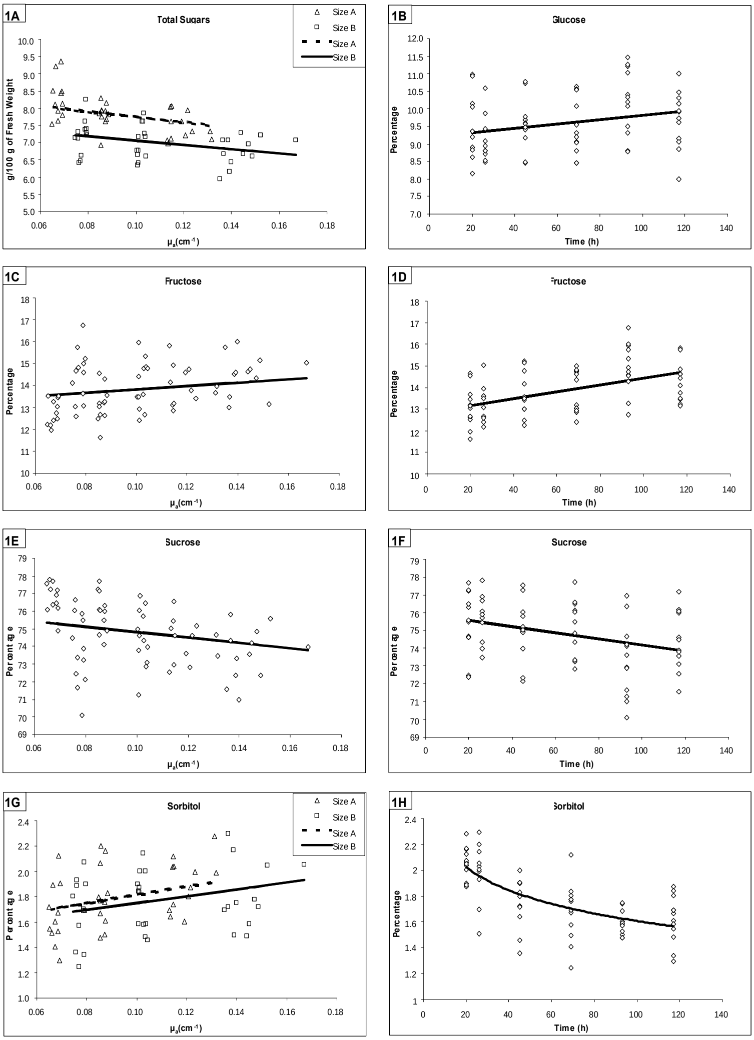

Figure 1. Predicted values of total sugars and percentages of glucose, fructose, sucrose and sorbitol from the regression parameters estimated in Table 1. Points are the observed data and lines are the predicted values

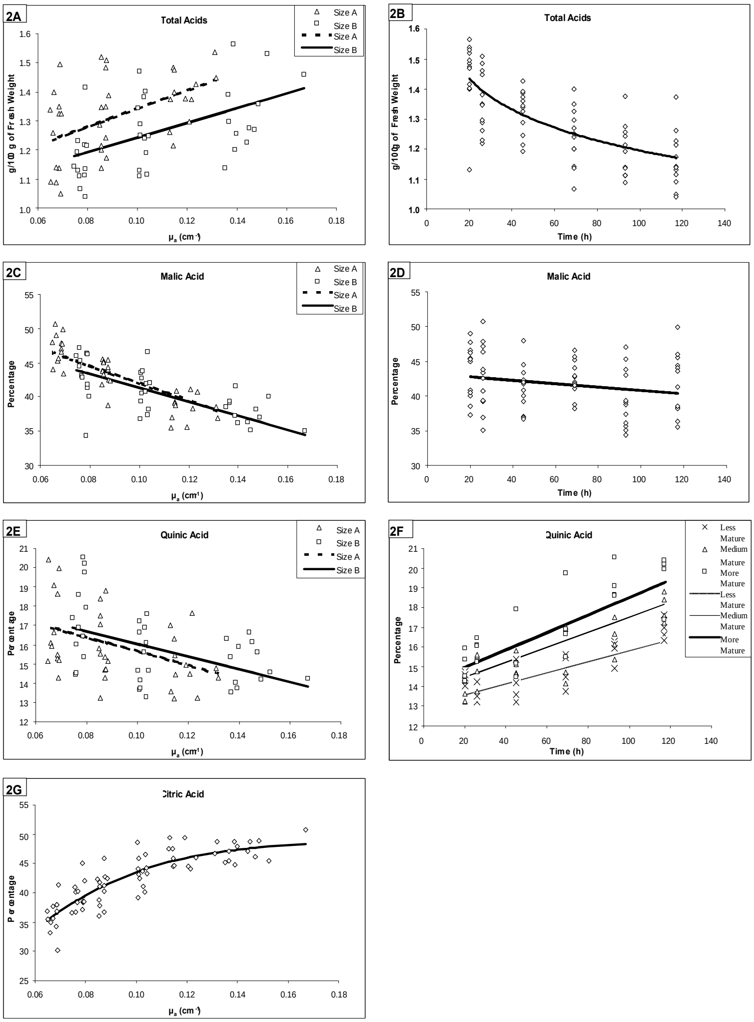

Figure 2. Predicted values of total acids and percentages of malic, citric and quinic acids from the regression parameters estimated in Table 1. Points are the observed data, and lines are the predicted values

On the other hand, differences in sugars or acids that are related to the amount of time the fruit are kept at 20°C are due to ripening during shelf life. In fruit that were mature and had a higher mass at harvest, the total sugars and the proportion of sucrose were higher, while the proportions of glucose and fructose were lower. This confirms that the total amount of sugars increased and that glucose and fructose were converted into sucrose while the fruit matured on the tree (Kobashi et al., 1999; Moriguchi et al., 1990).

During shelf life, this process was reversed. Sucrose was hydrolyzed to glucose and fructose without change in the total sugar content. In one study on peaches, this occurred only after four weeks of storage at 0°C, and did not occur during shelf life at 20°C (Robertson et al., 1990).

Sorbitol and sucrose are the main translocation products of photosynthesis (Bieleski and Redgwell, 1985). However, in our study, sorbitol was present in low amounts, whereas sucrose was present in high amounts. Both sorbitol and sucrose increased with increasing fruit mass. However, sorbitol decreased as the fruit matured, whereas sucrose increased. Therefore, Equation 1 can be used to predict the changes in sugar composition during early stages of fruit maturation, only if maturity at harvest time measured by μ_a at 670 nm is considered.

Total acids decreased both during the maturation of fruit on tree and during shelf life. The proportion of citric acid decreased and the proportion of malic acid increased with increasing fruit maturity at harvest time, which agrees well with previous studies (Meredith et al., 1989; Vanoli et al., 1993). In less mature fruit, citric acid was the most abundant organic acid, and malic acid the second most abundant organic acid. In more mature fruit, malic acid was the most abundant organic acid.

Acid composition may influence the consumer perception of fruit quality. Therefore, individual fruits can be sorted according to fruit quality by measuring μ_a at harvest time. Citric acid masks the taste of sucrose and fructose, whereas malic acid enhances the taste of sucrose (Schifferstein and Fritjers, 1990; Bonnans and Noble, 1993; Pangborn, 1963; Fabian and Blum, 1943). Our results indicate that fruit with a lower μ_a at harvest time could be perceived as sweeter because of the higher sugar content and the lower percentage of citric acid. On the other hand, fruit with a higher μ_a would be perceived as more sour.

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REFERENCES

Bassi D., Corelli Grappadelli L., Ravaglia G., Giusti I. 1995. Evoluzione della maturazione in due nettarine. Atti XXII Convegno Peschicolo, Cesena, Italy, 28-30 September 1995, pp. 66-70.

Bieleski R.L., Redgwell R.J. 1985. Sorbitol versus sucrose as photosynthesis and translocation products in developing apricot leaves. AUST. J. PLANT PHYSIOL. 12: 657668.

Bonnans S., Noble A.C. 1993. Effect of sweetener type and of sweetener and acid levels on temporal perception of sweetness, sourness and fruitiness. CHEM. SENSES. 18: 273-283.

Crisosto C.H. 1994. Stone fruit maturity indices: a descriptive review. POSTHARV. NEWS INFO. 5: 65n-68n.

Delwiche M.J., Baumgardner R.A. 1985. Ground colour as a peach maturity index. J. AMER. SOC. HORT. SCI. 110: 53-57.

Eccher Zerbini P., Spada G.L., Liverani C. 1994. Selection and experimental use of color charts as a maturity index for harvesting peaches and nectarines. ADV. HORT. SCI. 8: 107-113.

Eccher Zerbini P., Grassi M., Fibiani M., Rizzolo A., Biscotti G., Pifferi A., Torricelli A., Cubeddu, R. 2003. Selection of 'Springbright' nectarines by time-resolved reflectance spectroscopy (TRS) to predict fruit quality in the marketing chain. ACTA HORT. 604: 171-177.

Eccher Zerbini P., Vanoli M., Grassi M., Rizzolo A., Fibiani M., Biscotti G., Pifferi A., Torricelli A., Cubeddu R. 2005. Time-resolved reflectance spectroscopy as a non destructive tool to assess the maturity at harvest and to model the softening of nectarines. ACTA HORT. 682: 1459-1464.

Eccher Zerbini P., Vanoli M., Grassi M., Rizzolo A., Fibiani M., Cubeddu R., Pifferi A., Spinelli L., Torricelli A. 2006. A model for the softening of nectarines based on sorting fruit at harvest by time-resolved reflectance spectroscopy. POSTHARVEST BIOL. TECHNOL. 39: 223-232.

Fabian F.W., Blum H.B. 1943. Relative taste potency of some basic food constituents and their competitive and compensatory action. FOOD RES. 8: 179-193.

Forni E., Erba M.L., Maestrelli A., Polesello A. 1992. Sorbitol and free sugar contents in plums. FOOD CHEM. 44: 269-275.

Haji T., Yaegaki H., Yamaguchi M. 2004. Varietal differences in the relationship between maturation characteristics, storage life and ethylene production in peach fruit. J. JAP. SOC. HORT. SCI. 73(2): 97-104.

Kobashi K., Gemma H., Iwahori S. 1999. Sugar accumulation in peach fruit as affected by abscisic acid (ABA) treatment in relation to some sugar metabolizing enzymes. J. JAPAN SOC. HORT. SCI. 68: 465-470.

Moriguchi T., Sanada T., Yamaki S. 1990. Seasonal fluctuations of some enzymes relating to sucrose and sorbitol metabolism in peach fruit. J. AMER. SOC. HORT. SCI. 115: 278-281.

Meredith F.I., Robertson J.A., Horvat R.J. 1989. Changes in physical and chemical parameters associated with quality and postharvest ripening of harvester peaches. J. AGRIC. FOOD CHEM. 37: 1210-1214.

Pangborn R.M. 1963. Relative taste intensities of selected sugar and organic acids. J. FOOD SCI. 28: 726-733.

Rizzolo A., Vanoli M., Visai C. 1993. Effect of cold storage on volatile constituents of peaches and nectarines. ACTA HORT. 379: 467-473.

Robertson J.A., Meredith F.L., Horvat R.J., Senter S.D. 1990. Effect of cold storage and maturity on the physical and chemical characteristics and volatile constituents of peaches (cv Cresthaven). J. AGRIC. FOOD CHEM. 38: 620-624.

Schifferstein H.N.J., Fritjers J.E.R. 1990. Sensory integration in citrate/ sucrose mixtures. CHEM. SENSES. 15: 87-109.
Vanoli M., Visai C., Rizzolo A. 1993. Peach quality: influence of ripening and cold storage. ACTA HORT. 379: 445-450.

ZMIANY SKŁADU CUKRÓW I KWASÓW W NEKTARYNACH ‘AMBRA’ PODCZAS OBROTU TOWAROWEGO W ODNIESIENIU DO NIEDESTRUKCYJNEGO OKREŚLANIA DOJRZAŁOŚCI Z WYKORZYSTANIEM SPEKTROSKOPII FALI ODBITEJ W FUNKCJI CZASU

Usunięto: A

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STRESZCZENIE

Dojrzałość nektaryn podczas zbioru wpływa na cechy jakościowe owoców w trakcie obrotu towarowego, decydując o zadowoleniu konsumentów. Nowa niedestrukcyjna, optyczna metoda, spektroskopia fali odbitej w funkcji czasu (TRS), stosowana dla materiałów o wysokim stopniu rozproszenia optycznego, takich jak owoce, umożliwia pełną charakterystykę optyczną, przedstawioną w postaci współczynników absorpcji (μ_a) i odbicia (μ_s’). Stosunkowo wysokie wartości μ_a przy 670 nm, w pobliżu piku charakterystycznego dla chlorofilu, wiążą się z owocami mało dojrzałymi, podczas gdy niższe wartości μ_a wskazują na owoce bardziej dojrzałe.

Celem pracy było zbadanie zależności pomiędzy dojrzałością owoców podczas zbioru określaną z zastosowanie TRS, a składem cukrów i kwasów w nektarynach przetrzymywanych w temperaturze pokojowej. Nektaryny ‘Ambra’ zebrano w 2004 roku w okresie drugiego terminu zbioru handlowego i stosując TRS zmierzono μ_a przy 670nm. Owoce podzielono losowo na różne grupy reprezentujące pełen zakres μ_a. Analizowano zawartość ekstraktu (TSS), kwasowość miareczkową (TA) oraz skład cukrów i kwasów organicznych w owocach podczas zbioru i przetrzymywanych w temperaturze 20°C. Dane zostały przetworzone przy użyciu krokowej wieloczynnikowej regresji liniowej i wykazały, że μ_a był istotnie związany z zawartością cukrów i kwasów w owocach. Wraz ze zmniejszaniem się wartości μ_a, tj. w miarę dojrzewania owoców na drzewie, zwiększała się zawartość ekstraktu, cukrów ogólnych, procentowy udział sacharozy, kwasu jabłkowego i chinowego, a zmniejszał się procentowy udział fruktozy i sorbitolu, oraz ogólna zawartość kwasów, a szczególnie kwasu cytrynowego. W miarę wydłużania czasu przechowywania w temperaturze 20°C ogólna zawartość kwasów zmniejszała się, podczas gdy zawartość cukrów była bardziej stabilna. Podsumowując należy stwierdzić, że stosując spektroskopię fali odbitej w funkcji czasu i mierząc współczynnik μ_a przy 670 nm w momencie zbioru, można wyselekcjonować owoce o różnej jakości.

Słowa kluczowe: *Prunus persica* [L.] Batsch, nektaryny, dojrzałość, technika niedestrukcyjna, spektroskopia fali odbitej w funkcji czasu, związki rozpuszczalne, cukry, kwasy