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Quality evaluation of peaches and nectarines by electrochemical and multivariate analyses: relationships between analytical measurements and sensory attributes

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A propagation programme for peaches and nectarines has been targeted to select genotypes having taste attributes such as high sugar levels and well-balanced sugar/acid ratios. The analytical measurements of some soluble sugars and non-volatile acids were carried out using innovative analytical procedures based on fast and selective devices which require very little or no sample pre-treatment whatsoever. These devices have found a unique application in detecting fructose, glucose and malic acid for the improvement of fruit genetics.

The present study examines relationships between the analytical measurements of sugars and non-volatile acids and the sensory attributes (sweetness and sourness) of 21 peach and nectarine cultivars. Certain chemical parameters were correlated with the organoleptic acceptance of common commercial cultivars and recently introduced high and low-acid genotypes. Multivariate statistical analyses were found to be useful in describing the variability of the chemical and sensory parameters which characterise peach quality, as they enabled the identification of sets of variables that could be used to classify peaches and nectarines into high and low-acid categories. Malic and citric acids, minor components of these fruits, were important taste attributes as they contributed to the sensory perception of sourness. © 1997 Elsevier Science Ltd

INTRODUCTION

Quality was defined by Kramer & Twigg (1966) as being composed of those chemical and physical characteristics that give a product consumer appeal and acceptability.

Skin appearance (colour and freedom from defects), texture, flavour and volatile compounds, and sugar and acid content are key factors that determine high-quality fresh peaches and nectarines. Studies made on these quality-defining parameters for peaches and nectarines are reported in the literature (Robertson *et al.*, 1988; Shewfelt *et al.*, 1987). It is the combination of sugars, acids, flavours, tannins and certain physical properties of the pulp that gives fruit taste (Bellini *et al.*, 1994; Sistrunk *et al.*, 1979). According to Hesse (1975), fruit taste and sweetness are well correlated with quality by consumers.

Bourne (1979) outlined that, due to the high variations in fruit, there were difficulties involved in correlating analytical and sensory measurements. Nevertheless, Dever *et al.* (1995) examined the sources of variations that affect the assessment of whole apple fruit quality and the multivariate relationships between analytical and sensory characteristics.

The objective of this study was to examine relationships between the analytical measurements of both sugars and non-volatile acids and the sensory attributes (sweetness and sourness) of a sample of 21 cultivars of peaches and nectarines at eating ripeness.

In order to improve the organoleptic quality of peach and nectarine cultivars, according to consumer accep-

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tance, a propagation programme was recently started up with the aim of producing genotypes with excellent taste, high sugar levels, and balanced sugar/acid ratios. The analytical measurements of certain soluble sugars and non-volatile acids were carried out using electrochemical biosensors, innovative measuring devices requiring very little or no sample pre-treatment whatsoever that which are highly selective and reproducible (Mascini & Palleschi, 1989). These devices, based on amperometric measurements, have a response time of 1–2 min and can be miniaturised, constructed and used as disposable sensors. In this study, glucose, fructose and malic acid probes were also used to improve the genetics of the fruit, with good results.

Certain chemical parameters were correlated with the organoleptic acceptance of well-known genotypes that have recently been introduced.

MATERIALS AND METHODS

Peach and nectarine fruit

Twenty-one early-to-late maturing peach and nectarine cultivars (Table 1) were obtained from the experimental orchards of the Istituto Sperimentale per la Frutticoltura (Fiorano, Rome, Italy). 'Babygold 9', 'Grezzano', 'Iris Rosso', 'Maria Aurelia', 'Snow Queen', 'Spring Star', 'Super Crimson Gold' and 'Venus' are all widely grown commercial cultivars with high-acid genotypes. In addition, 13 recently introduced cultivars, which could be used to improve the Italian varieties, were selected:

1. High-acid genotypes: 'Argento di Roma', 'Morsiani 51' and 'Oro A'.
2. Low-acid genotypes: 'Beauty Lady', 'Big Top', 'Douceur', 'Felicia', 'Lucie', 'Royal Glory', 'Sensation' and 'Sweet Lady'.
3. Low-acid genotypes with a 'honey taste': 'Kurakata Wase' and 'Yumyeong'.

The trees were about 4 years old, grafted on the same rootstock, spaced at 4.5 m × 2.5 m and trained as spindle. The fruits of each cultivar were hand-picked from three trees at eating ripeness. Twenty fruits with the same diameter, skin colour and firmness to the touch were selected as representative samples and divided into two groups for chemical and sensorial analyses (15 and five fruits, respectively). They were analysed within 24 h of being harvested.

Chemicals

Glucose oxidase (EC 1.1.3.4; from *Aspergillus niger*, type VII), fructose dehydrogenase (EC 1.1.99.11; from *Gluconobacter* sp.), L-malic acid (sodium salt) and malic enzyme (EC 1.1.1.40, 26 units mg^{-1}; from chicken liver) were purchased from Sigma Chemical Co. (St Louis, MO, USA). Ferricyanide was from Boehringer (Mannheim, Germany) and pyruvate oxidase (EC 1.2.3.3, 20.7 units mg^{-1}; from *Pediococcus* sp.) was from Toyo Iozo (Shisuoka, Japan). Cellulose acetate membrane (100 nominal molecular weight cut-off) was prepared in our laboratory according to a procedure reported by Mascini *et al.* (1987). Microporous polycarbonate membrane (0.03 μm) was obtained from

Table 1. Peach and nectarine cultivars used in this study

Cultivar	Description of fruit	Fruit genotype	Ripening ± Redhaven
Widely grown commercially			
'Babygold 9'	Y, Pc	High-acid	42
'Grezzano'	W, P	High-acid	−5
'Iris Rosso'	W, P	High-acid	−9
'Maria Aurelia'	Y, N	High-acid	23
'Snow Queen'	W, N	High-acid	−15
'Spring Star'	Y, N	High-acid	−14
'Super Crimson Gold'	Y, N	High-acid	−15
'Venus'	Y, N	High-acid	25
Recently available on the market			
'Argento di Roma'	W, N	High-acid	−14
'Beauty Lady'	W, P	Low-acid	−5
'Big Top'	Y, N	Low-acid	2
'Douceur'	W, P	Low-acid	58
'Felicia'	W, P	Low-acid	−12
'Kurakata Wase'	W, P	Low-acid	−10
'Lucie'	Y, P	Low-acid	62
'Morsiani 51'	Y, N	High-acid	37
'Oro A'	Y, Pc	High-acid	−15
'Royal Glory'	Y, P	Low-acid	−10
'Sensation'	Y, P	Low-acid	35
'Sweet Lady'	Y, N	Low-acid	40
'Yumyeong'	W, P	Low-acid	34

P, peach; N, nectarine; Pc, canning peach; W, white; Y, yellow.

Table 2. Analytical performances of the biosensors

Sensor	Lower detection limit (mol litre^{-1})	Upper detection limit (mol litre^{-1})	Linearity range (mol litre^{-1})	Relative standard deviation (%)
Glucose	5×10^{-7}	2×10^{-3}	1×10^{-6}–1×10^{-3}	2.2
Malate	5×10^{-7}	1×10^{-3}	1×10^{-6}–5×10^{-4}	1.7
Fructose	1×10^{-6}	5×10^{-4}	5×10^{-6}–1×10^{-4}	3.4

Nucleopore (Pleasanton, CA, USA), the Immobilon-AV affinity membrane (0.65 μm pore size, 125 μm thick) was from Millipore (Bedford, MA, USA) and the Immunodyne immunoaffinity membrane was from Pall Corp. (Glen Cove, NY, USA).

Water and acetonitrile were of HPLC-purity grade, other reagents were of analytical grade; all were obtained from Farmitalia C. Erba (Milan, Italy).

Apparatus

Electrochemical measurements were carried out with an ABD (amperometric biosensor detector) from Universal Sensors (Metaire, LA, USA). The probe used for batch analysis was a hydrogen peroxide electrode from Universal Sensors. Currents were recorded with a Model 868 AMEL recorder (Milan, Italy).

Sucrose, fructose and glucose reference measurements were carried out using a high-performance liquid chromatography (HPLC) method. The system consisted of a Waters HPLC system, with a Model 600E solvent delivery system, a Model 410 differential refractometer detector and a Rheodyne 7125 injector (loop of 20 μl). A Waters carbohydrate analysis column (3.9 mm× 300 mm) at 30°C was used. The mobile phase consisted of acetonitrile–water (80:20, v/v) at a flow rate of 0.8 ml min^{-1}.

Chemical analysis

Fifteen peaches from each cultivar were divided into three replications of five fruits each. The fruits were sliced and stoned and the slices were ground to a puree in a Waring blender. The homogenate was filtered and the juice obtained was analysed. The juice samples were filtered through a 0.4 mm Millipore filter for HPLC analysis. Glucose, malate and fructose determinations were carried out using electrochemical biosensors. The electrochemical transducer used to determine glucose and malic acid content was a H_2O_2 platinum electrode maintained at +650 mV applied potential versus a silver/silver chloride cathode.

The reactions were as follows:

Glucose:

$$\text{Glucose} + O_2 \xrightarrow{\text{Glucose oxidase}} \text{Gluconic acid} + H_2O_2$$

Table 3. pH, soluble sugar and non-volatile acid composition (g per 100 g fresh weight) of 21 peach and nectarine cultivars

Cultivar	pH	Sucrose	Glucose	Fructose	Malic acid	Citric acid
'Baby Gold 9'	4.1	8.8	0.8	1.2	0.6	0.2
'Grezzano'	4.0	7.0	0.6	0.8	0.5	0.1
'Iris Rosso'	3.5	4.3	0.9	1.0	0.4	0.6
'Maria Aurelia'	4.1	7.3	0.8	1.1	0.4	0.6
'Snow Queen'	3.9	5.7	0.8	1.3	0.5	0.5
'Spring Star'	3.6	9.4	1.4	1.9	1.0	0.5
'Super Crimson Gold'	3.7	8.2	1.0	1.1	0.9	0.6
'Venus'	4.1	7.4	1.6	2.2	0.7	0.4
'Argento di Roma'	3.6	4.4	0.9	1.1	0.4	0.5
'Beauty Lady'	3.9	8.3	0.5	0.7	0.6	0.3
'Big Top'	4.5	8.6	0.9	1.3	0.5	0.4
'Douceur'	4.4	9.8	0.7	0.8	0.4	0.0
'Felicia'	4.6	9.3	0.5	0.5	0.2	0.2
'Kurakata Wase'	4.4	6.9	0.6	0.8	0.2	0.2
'Lucie'	3.9	6.4	0.8	1.0	0.7	0.2
'Morsiani 51'	4.1	5.8	1.6	1.9	0.5	0.6
'Oro A'	3.8	7.7	0.4	0.4	0.6	0.2
'Royal Glory'	4.0	6.7	0.8	0.9	0.4	0.1
'Sensation'	4.7	4.6	2.0	3.4	0.3	0.2
'Sweet Lady'	4.2	5.5	1.3	2.1	0.5	0.4
'Yumyeong'	4.9	8.8	1.8	2.5	0.2	0.1

Values are the averages of triplicate samples.

Malate:

$$\text{L-Malate} + \text{NADP}^+ \xrightarrow{\text{Malic enzyme}} \text{Pyruvate} + \text{NADPH} + \text{CO}_2 + \text{H}_+$$

$$\text{Pyruvate} + \text{HPO}_4^{2-} \xrightarrow{\text{Glucose oxidase}} \text{Acetylphosphate} + \text{H}_2\text{O}_2 + \text{CO}_2$$

The procedures for assembling the glucose and malate probes and the analyses of glucose and malate were the same as those used in previous studies (Mascini *et al.*, 1988; Matsumoto *et al.*, 1988; Palleschi *et al.*, 1989; Palleschi *et al.*, 1990; Messia *et al.*, 1996).

The working electrode used to determine fructose was a platinum electrode maintained at +250 mV versus a built-in silver/silver chloride reference electrode. The probe was assembled by placing the following membranes on an inverted electrode jacket:

- Immobilon AV affinity membrane with fructose deydrogenase on its surface.
- 0.03 μm polycarbonate membrane.

The reaction was as follows:

$$\text{Fructose} + \text{Mediator}_{\text{OX}} \xrightarrow{\text{Fructose dehydrogenase}} \text{Ketofructose} + \text{Mediator}_{\text{RED}}$$

$$\text{Mediator}_{\text{RED}} \xrightarrow{\text{Electrode}} \text{Mediator}_{\text{OX}}$$

Measurements were carried out in a 0.1 M phosphate buffer, pH 7.0, using potassium ferricyanide ($K_3Fe(CN)_6$), 1.5 mmol litre^{-1}, as the mediator.

The enzymes were immobilised on the membranes according to a procedure reported in the literature (Palleschi *et al.*, 1994; Messia *et al.*, 1996).

Spectrophotometric determination of citric acid was carried out using Kit No. 139076 from Boehringer Mannheim (Germany).

A special ISFET-based pH-probe (pH-System 1001; Sentron, Roden, The Netherlands), constructed for direct pH measurement into semi-solid matrices, was inserted into the fruits to measure the pH.

Sensory analysis

A semi-trained sensory panel (ten assessors) completed two replicated evaluations of five fruits from each genotype, for sweetness, sourness and fruity flavour, on an intensity scale ranging from 1 (none) to 7 (high intensity). The term 'fruity flavour' was defined as the characteristic aromatic-rich flavour of peach that may exist in addition to, but independent of, the sweet taste.

Each fruit was peeled and cut into quarters. Differences in sensory evaluation must be considered to be due to variations in ripeness between the top and the bottom of peaches and in sugar and organic acid content. For this reason, each assessor was given a uniform longitudinal section of the entire height of the fruit. The peaches were peeled and trimmed immediately prior to presentation so that colour and oxidative browning would not influence the evaluations. Random genotype samples and their replicates were given to the assessors in different sequences and the tests were performed at room temperature in individual tasting booths under normal lighting.

Statistical analysis

Data on both assessors and replications were averaged for sensory data, whereas only data on the replications were averaged for the analytical data.

In order to find the main variation trends between chemical and sensory variables in the peach genotypes and to evaluate their correlation, data were processed according to Principal Components Analysis (PCA) (Piggott & Jardine, 1986) using a SIMCA program (Wold, 1987). The cross-validation procedure (Wold, 1978) was used to determine the maximum number of significant dimensions to avoid data over-fitting.

RESULTS AND DISCUSSION

Analytical optimisation

Calibration curves of glucose, malate and fructose, carried out with electrochemical biosensors, led to the results reported in Table 2, which shows the lower and upper detection limit, the linearity range and the relative standard deviation calculated on three consecutive measurements at a fixed standard concentration and with selected samples of fruit. The probes gave good reproducible results. Calibrations were performed during fruit analysis, and both stability and drift probes were evaluated. The sensitivity of the probes enabled a dilution of 1/500, 1/200 and 1/1000 for glucose, malate and fructose, respectively.

The stability of the probes was excellent; probe drift, calculated over 1 day, gave a relative error of less than 1%, which is totally compatible with the accuracy of the analysis since the calculation for relative error was 3–5%.

Soluble sugar and non-volatile acid composition

The sucrose, glucose and fructose content—the three predominant sugars and major contributors to sweetness in many peach and nectarine cultivars (Byrne *et al.*, 1991)—were examined. The results showed substantial variations between cultivars (Table 3). Sucrose was the major soluble sugar in the genotypes examined, which supports the findings of other studies (Chapman *et al.*, 1991). Almost all the genotypes had higher fructose than glucose content.

Major differences in the non-volatile acid levels of peach and nectarine genotypes (Table 3) were found. Only malic and citric acids were examined in this study, being the dominant acids in many peach and nectarine cultivars (Wills *et al.*, 1983). In all the genotypes, malic acid was not always found in greater quantities than citric acid. Increasing malic to citric acid ratios were also observed in all the cultivars as they ripened. Several studies suggest that this ratio could be used as an index of maturity (Meredith *et al.*, 1989; Chapman & Horvat, 1990).

Multivariate analysis

A summary of the total variation of both sensory and chemical variables is presented by their factor loadings

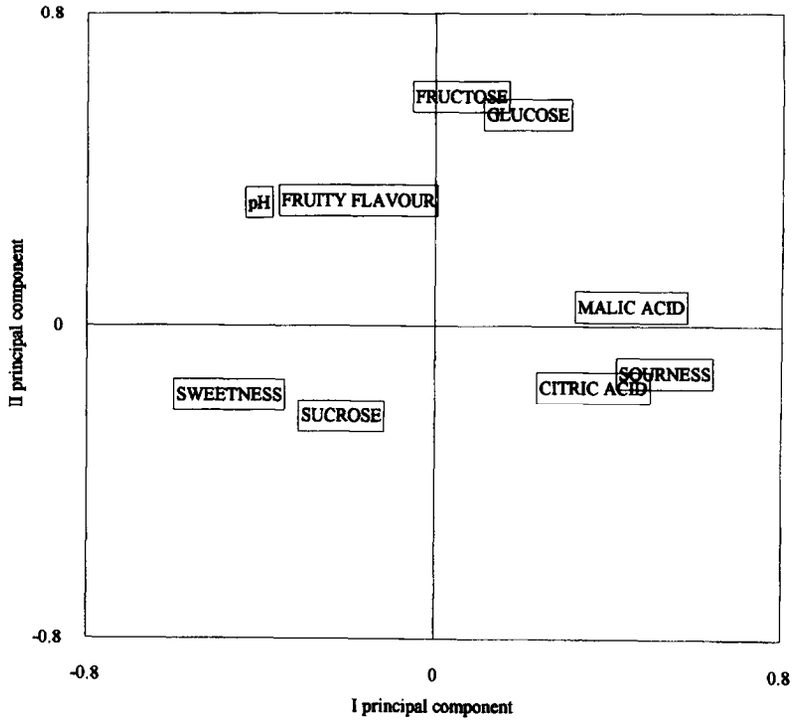

Fig. 1. PCA loadings for dimensions 1 and 2.

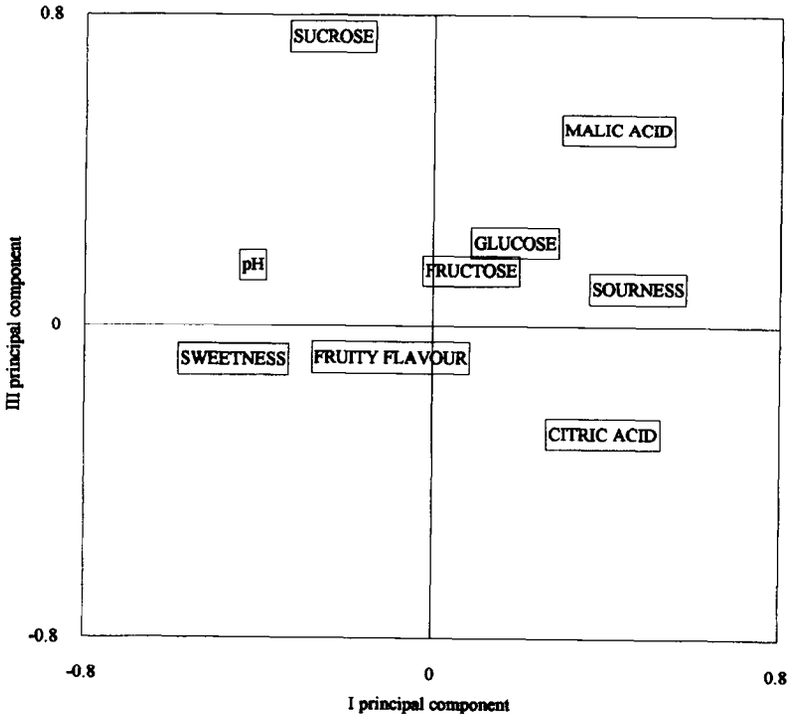

Fig. 2. PCA loadings for dimensions 1 and 3.

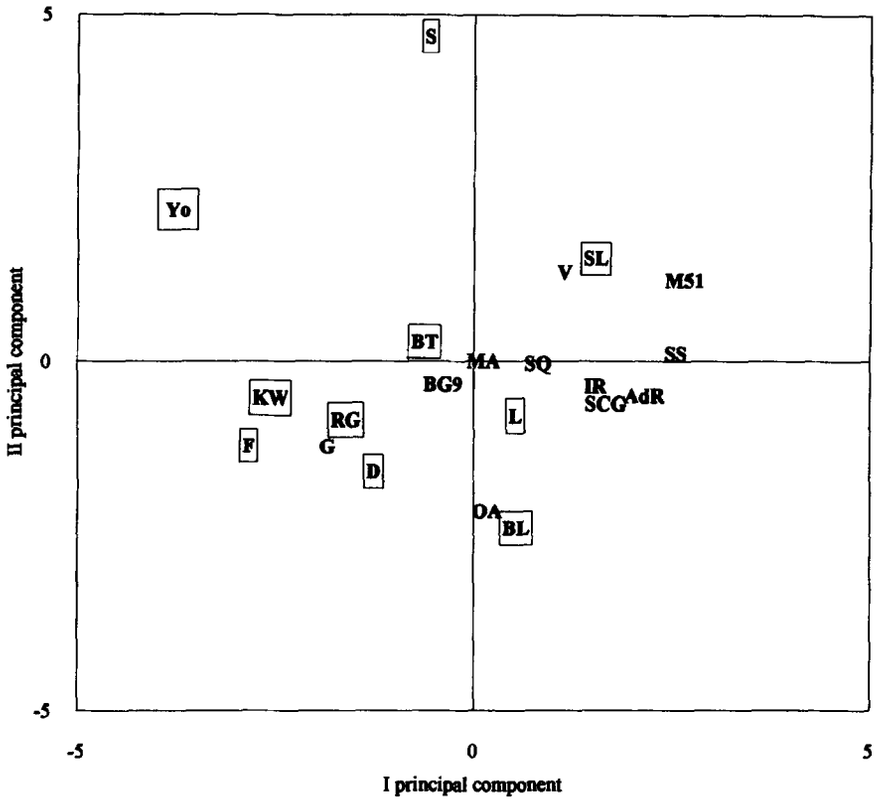

Fig. 3. Score plot of peach and nectarine genotypes by the dimensions 1 and 2 from PCA: 'Babygold 9' (BG9), 'Grezzano' (G), 'Iris Rosso' (IR), 'Maria Aurelia' (MA), 'Snow Queen' (SQ), 'Spring Star' (SS), 'Super Crimson Gold' (SCG), 'Venus' (V), 'Argento di Roma' (AdR), 'Beauty Lady' (BL), 'Big Top' (BP), 'Douceur' (D), 'Felicia' (F), 'Kurakata Wase' (KW), 'Lucie' (L), 'Morsiani 51' (M51), 'Oro A' (OA), 'Royal Glory' (RG), 'Sensation' (S), 'Sweet Lady' (SL), 'Yumyeong' (Yo).

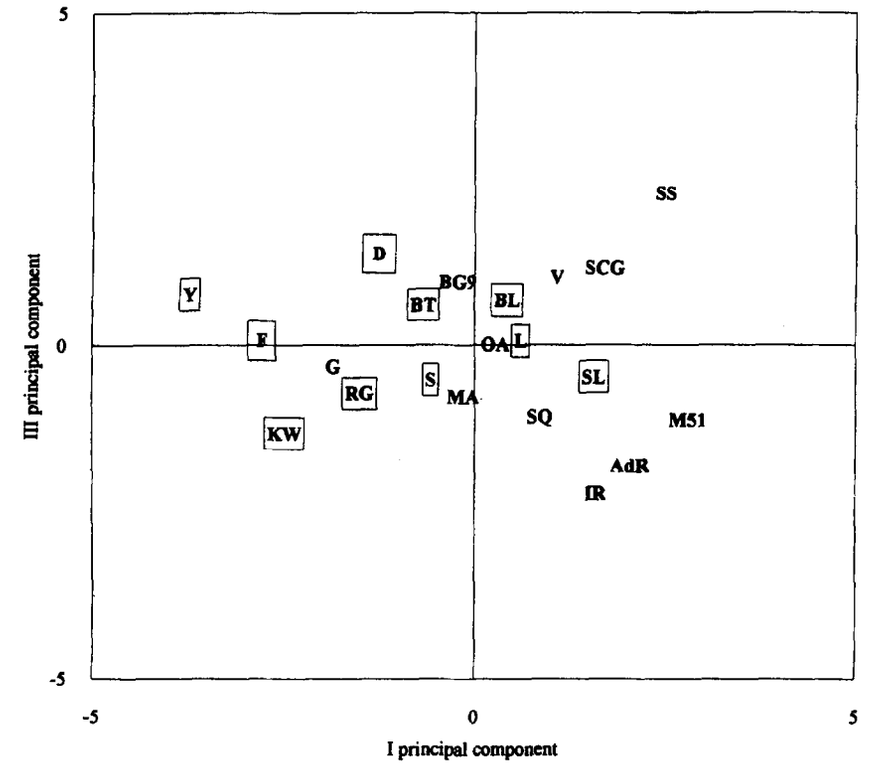

Fig. 4. Score plot of peach and nectarine genotypes by the dimensions 1 and 3 from PCA: 'Babygold 9' (BG9), 'Grezzano' (G), 'Iris Rosso' (IR), 'Maria Aurelia' (MA), 'Snow Queen' (SQ), 'Spring Star' (SS), 'Super Crimson Gold' (SCG), 'Venus' (V), 'Argento di Roma' (AdR), 'Beauty Lady' (BL), 'Big Top' (BP), 'Douceur' (D), 'Felicia' (F), 'Kurakata Wase' (KW), 'Lucie' (L), 'Morsiani 51' (M51), 'Oro A' (OA), 'Royal Glory' (RG), 'Sensation' (S), 'Sweet Lady' (SL), 'Yumyeong' (Yo).

Table 4. Explained variances (%), total and residual variances after three statistically significant principal components (I–III)

	I	II	III	Total	Residual
pH	51.6	25.4	2.8	79.8	20.2
Sucrose	10.1	9.2	80.6	99.9	0.1
Glucose	1.4	84.9	13.6	99.9	0.1
Fructose	<0.1	92.5	7.5	100.0	<0.1
Malic acid	43.5	2.4	33.2	79.1	20.9
Citric acid	56.8	<0.1	2.5	59.3	40.7
Sweetness	64.8	8.2	<0.1	73.0	27.0
Fruity flavour	<0.1	24.8	<0.1	24.8	75.2
Sourness	75.2	3.5	<0.1	78.7	21.3
Total variance	36.0	27.9	17.2	81.1	18.9

from the first three factors of the PCA (Figs 1 and 2). This method enables the main relationships between the variables to be revealed.

Three dimensions of the PCA model were found to be significant and explained the 81% fraction of variance. The explained variances for each principal component, and the total and residual variances after three dimensions, are shown in Table 4 for each variable. The first component, accounting for 36% of the total variance, is essentially an acid/sour versus sweet dimension. It was dominated by malic and citric acids and sourness (positively loaded), pH and sweetness (negatively loaded). Sucrose content also contributed to the variance this factor described. The second dimension, accounting for 27.9% of the total variance, showed that glucose and fructose were the main contributors and explained a high proportion of variance (84.9% and 92.5%, respectively). Finally, a third dimension, accounting for 17.2% of the total variance, was dominated by sucrose content and explained the additional variance for malic acid.

Fruity flavour, with only 24% of variance, explained by the second component, poorly discriminated the samples.

The PCA scores of samples on the 1 and 2 and the 1 and 3 dimensions are given in Figs 3 and 4, respectively. The first dimension was most effective in discriminating between the low-acid cultivars (squared in the plot), distributed on the negative half of the first component, and the high-acid cultivars on the positive side. Only 'Beauty Lady' (BL), 'Lucie' (L) and 'Sweet Lady' (SL), with low positive scores on the first dimension, had a less pronounced low-acid character.

Correlations between analytical and sensory variables

The PCA solution demonstrates that there is a relation between chemical and sensory measurements. Along the first component, the peach and nectarine genotypes are separated on the basis of acids/sourness, sucrose/sweetness and pH.

The genotypes with low malic and citric acid content were perceived to be less sour, and therefore their sweetness does not seem to depend only on soluble sugar content.

Correlation coefficients between certain analytical and sensory variables were also evaluated (Kader *et al.*, 1982); significant correlations were found for malic acid versus sourness ($R = 0.575$; $P < 0.01$), citric acid versus sourness ($R = 0.582$; $P < 0.01$) and for pH versus sourness ($R = -0.612$; $P < 0.01$). On the other hand, no significant correlations were found between sucrose content and sweetness ($R = 0.388$), which means that the high level of sweetness perceived in the low-acid genotypes is not correlated to high sucrose content but to low malic and citric acid content.

CONCLUSION

Multivariate statistical analyses were effective in describing the chemical and sensory variables which characterise peach quality, as they enabled the identification of sets of variables that could be used to divide peaches into low-acid categories. Moreover, the scores of three low-acid genotypes—namely, 'Beauty Lady' 'Sweet Lady' and 'Lucie'—showed that they veered away from their type, and they therefore had a less pronounced low-acid taste. Malic and citric acids, minor components of the fruit, were important taste attributes as both contributed to the sensory perception of sourness.

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