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Plum-tasting using near infra-red (NIR) technology**

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A b s t r a c t. This paper concerns the feasibility of using near infra-red (NIR) technology for tasting fruit. The aim is to improve a non-destructive method related to the development of taste components (other than sugar content and acidity) for detecting characteristic taste parameters in different commodities. Such sensors can be used online in fruit-grading (according to their taste quality) in warehouses and public fruit markets. In this research, a NIR spectrometer with photo diode array (PDA) detector, was able to classify two varieties of plums (Reine Claude and Blackamber) which had the same ratio of soluble solid contents (SSC) and acidity. The non-destructive classification was based on optical reflectance within NIR range (700-1100 nm). Both Reine Claude and Blackamber were correctly classified in 92.8% of the cases at 5% significant level, which indicates that NIR technology has high potential for plum tasting.

K e y w o r d s: NIR, quality, non-destructive, taste, classification

INTRODUCTION

In recent years, research has focused on the development of non-destructive techniques for measuring quality parameters of different commodities. NIR spectroscopy is one of these techniques. NIR spectroscopy is particularly sensitive to the presence of molecules containing the C-H, O-H, and N-H groups. These bonds interact in a measurable way in the NIR portion of the spectrum, thus constituents such as starch and sugars (C-H), alcohols, moisture and acids (O-H), and protein (N-H) can be quantified in solids, liquids and slurries. In addition, an analysis of gases is possible. NIR is not a trace analysis technique and is generally used for measuring components that are present at concentrations greater than 0.1%. NIR creates a faster, safer working environment and does not require chemicals (Ozanich, 1999).

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There were many contributions in the field of NIR spectroscopy used for assessing some quality parameters of fruits and vegetables; such as: pH, sugar content, firmness, texture parameters, optimum picking date, light penetration of NIR in fruit and bruising (Lammertyn *et al*., 2000). To our knowledge, taste is an issue that is not often discussed in the literature.

NIR ranges were different from one contribution to another. In this experiment, wavelengths between 700-1100 nm were used. NIR in this range is promising and more useful for intact foods due to the following facts (Carlini *et al.*, 2000; McGlone and Kawano, 1998; Walsh *et al*., 2000):

1. Radiation can penetrate much further in fruit of many different species.
2. Water absorbance peaks are less strong and broad and the risk is low of masking spectral information correlated to low concentration constituents.
3. The corresponding instrumentation is low cost, suitable for process control and portable enough for 'in situ' field measurements.
4. The bands are ascribed to the third and forth overtones of O-H and C-H stretching modes and are expected to be separated due to disharmony.
5. Lower absorbance at these wavelengths allows transmission optics.

Optical measurements can be done in different modes: transmittance, absorbance and reflectance. Optical reflectance was used in this research. Chen (1978) stated that reflectance is generally easier to use for the quality evaluation of agricultural products due to:

1. Its relative high intensity: since reflectance in the visible and infrared regions ranges up to 80% of the incident energy; and

2. Reflectance measurement is not adversely affected by low-intensity background light.

Taste is an important internal quality of a commodity. The taste of any fruit is considered to be composed of SSC, acidity and characteristic taste parameters (distinguished chemicals) of the fruit. The basis for this work is that, if it is possible using NIR technology, to classify two different varieties (of the same commodity) having the same SSC/acidity values, then NIR can detect the characteristic taste parameters in both varieties.

METHODOLOGY

Fruit

Two varieties of plum, Reine Claude (*Prunus domistica*) and Blackamber (*Prunus silicina*), eighty of each variety were used. The plums were mature and of uniform surface. They were obtained from a local supplier in August. After being in cold store, the plums were kept at room temperature (20^{o}C) for 24 h for equilibration before the experiment.

Reflectance measurements

A scanning Zeiss MMS1 NIR enhanced spectrometer was used to collect reflectance readings over a wavelength range of 700-1100 nm in 2 nm increments, yielding 200 values per spectrum. For each variety, the reflectance measurements were done in one day. For each plum, three reflection spectra were taken at three equidistant positions around the equator in order to eliminate spatial variability. The light source consisted of a 12V/100W tungsten halogen lamp. Calibration of the lamp, using a plate made of $BaSO_4$, was done twice during reflectance measurements of each variety, to guarantee the stability of the lamp. The light passed through a bundle of optical fibers to the fruit, and the reflected light was transferred to a photo diode array (PDA) detector through another bundle of fiber optics. A holder was designed to support the plums and direct the light at a 45 degree angle to the plums (to avoid specular reflectance), and maintain a distance of 1 cm between the probe and the plums. The integration time (time needed for a spectrum to be acquired) was 181 ms (milliseconds). Each reflectance spectrum used in multivariate analysis was an average of the three spectra obtained for each plum.

Chemical analysis

1. Soluble solid contents (SSC): A digital refractometer (RFM 90-Struers) was used to measure the SSC of the plums' juice. The SSC was expressed in Brix; and

2. Titrateable acidity (citric acid): A 719 S Titrino was used for measuring titrateable acidity. Plum juice acidity was obtained by titrating the juice with 0.1 M NaOH to a pH 8.1 endpoint.

Multivariate analysis

The calculations were carried out using 'Unscrambler' v. 7.5 (CAMO, ASA, Oslo, Norway), a statistical software package for multivariate analysis. Matlab R.12 (The Math Works Inc., Natick, MA) was used as a bridge program between the spectrometer outputs and Unscrambler to transfer the reflectance data to be analyzed. The spectra analysis (modelling and classification) was based on full multiplicative scatter correction (MSC) transformed data. The partial least square (PLS) technique was used for modelling. The soft independent modelling of class analogies (SIMCA) classification technique was used for the classification plums according to their reflectance spectra. In the SIMCA classification technique, the classification succeeds when there are very clear distinguished groups of the classes targeted (two varieties in this research) in the different SIMCA pertinent graphs (Esbensen *et al*., 2000). Samples are considered wrongly classified when they do not belong to any of the models of the classes targeted. SIMCA classification tables were used for expressing the classification percentages of different varieties.

Principles of classification

Fruit taste being the major asset of fruit quality is dominated by the sugar to acid ratio (Blanke, 1996). Groups of plums, which have the same SSC/acidity values, were gathered for classification. Having the same ratio of SSC and acidity means that both components (sugar and acidity) are eliminated leaving only the characteristic taste parameters of the variety to be detected. Investigating the possibility of classifying these groups will open a wide range for studying and investigating characteristic taste parameters other than SSC and acidity.

RESULTS

The averaged values of SSC and acidity for each variety of plum is tabulated in Table 1.

The SSC between the two varieties was significantly different, while acidity was insignificant between the two varieties at 5% significant level. The correlation between acidity and SSC was very low.

All the spectra analysis (modelling and classification) was based on full multiplicative scatter correction (MSC) transformed data, since it was found that full MSC preprocessing technique describes the data better than the raw data itself or first and second derivative pre-processing techniques.

In the reflectance spectra score plot of all plum samples (from both varieties), the first principal component (PC) describes 68% of the variation between all samples (Fig. 1).

T a b l e 1. Chemical reference values of Reine Claude and Blackamber plums

Variety	SSC (Brix)				Acidity (g/100 g)			
	Average	SDev*	CV*	Range	Average	SDev	CV	Range
Reine Claude	11.54	2.21	19%	7.5-16.5	1.05	0.43	41%	0.10-1.97
Blackamber	8.55	1.77	21%	4.5-12.3	1.06	0.20	19%	0.53-1.57

*SDev: - Standard Deviation, *CV - Coefficient of Variation = SDev / Average.

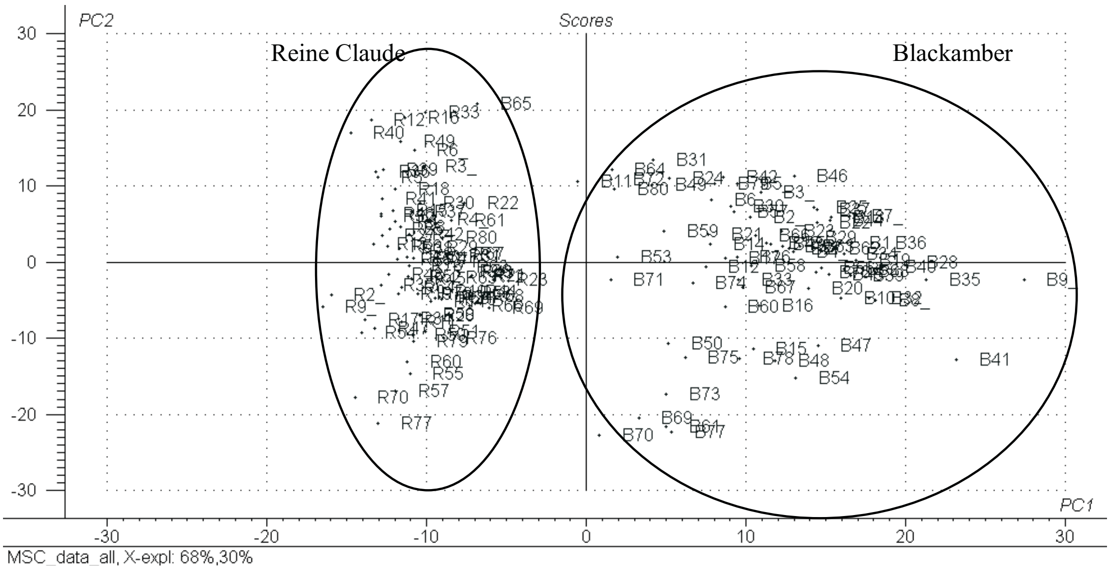

Fig. 1. Reflectance spectra scores (MSC pre-processed) plot of all plum samples (R: Reine Claude samples, B: Blackamber samples. The number followed the letter is the sample series number).

The partial least square (PLS) method was used for modelling SSC for both varieties, 100 and about 60 samples were used for calibration and validation, respectively. SSC has a validation correlation coefficient of 79.9% and a root mean square error of prediction (RMSEP) of 1.56 with four PCs. Figure 2 shows PLS model for SSC. It was found that the most important NIR ranges for modeling SSC were 778-810, 902-935 and 960-990 nm. Acidity modeling was not satisfactory, the validation correlation coefficient was very low.

The SIMCA technique was used for the classification process. For classifying all the plum samples (160 samples), a training set containing 50 samples and a test set containing 30 samples from each variety were used. Reine Claude and Blackamber were correctly classified in 90 and 96.6% of the cases, respectively at a 5% significant level as shown in Table 2.

Cooman's plot is shown in Fig. 3. Cooman's plot shows the objects at the model distance for both the new objects (test set) and the calibration objects (training set). The numbers on the x and y-axis are residual to the two groups. One coordinate is given for each sample, which is the summed square over all variable residuals for that component.

Samples of plums having the same values of SSC/acidity, within ±5%, were approximately 30 samples from each variety (63 samples from both varieties). The mean reflectance spectra of these samples (Fig. 4) are significantly different.

Also, the score plot of the reflectance of these samples (Fig. 5) shows clearly distinguished groups (two varieties) along the first principal component. The first principal component explains 90% of the variation between the samples.

For classifying samples having the same values of SSC/acidity, 35 samples from both varieties were used in the training set. The reflectance spectra of the rest (28 samples) were used in the test set. Results at 5% significant level are shown in Table 3.

Cooman's plot is shown in Fig. 6.

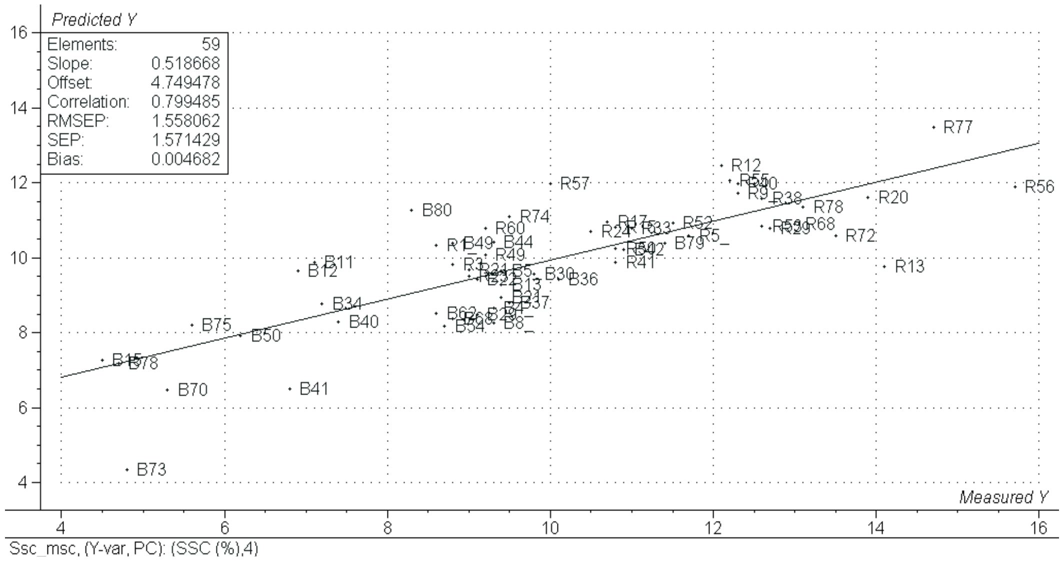

Fig. 2. PLS modelling for SSC of all plum samples.

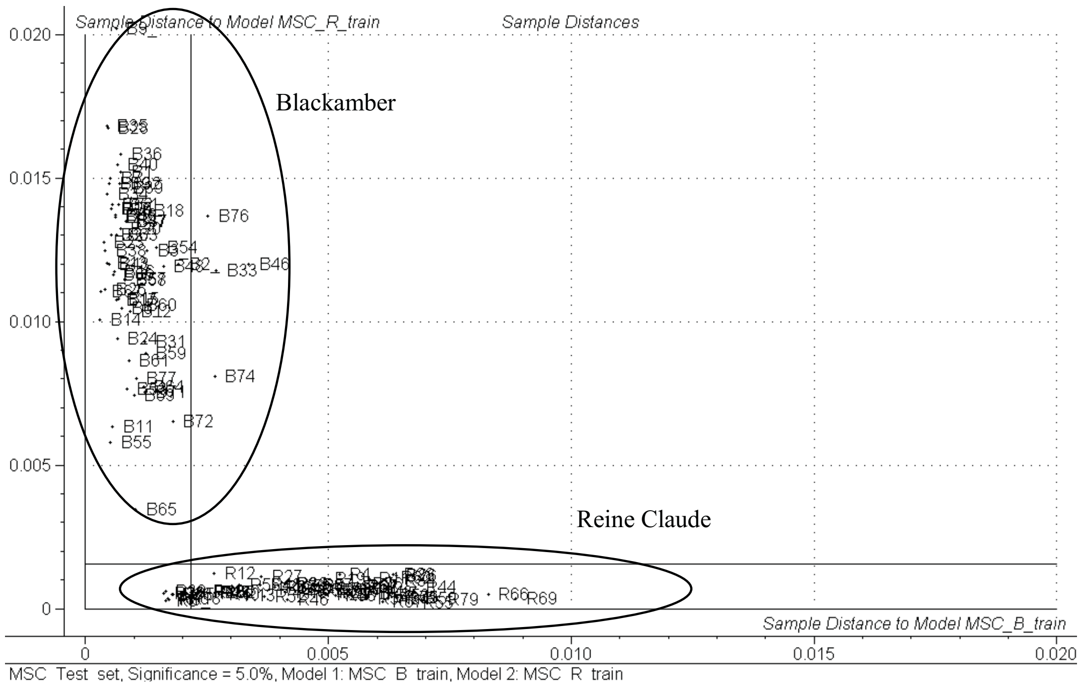

Fig. 3. Coomans plot for all Blackamber and Reine Claude samples at 5% significant level (Dark gray: train set, light gray: test set).

T a b l e 2. Classification result of NIR reflectance spectra for two varieties of plums

Variety	Reine Claude	Blackamber	Error
		(%)	
Reine Claude	90	0	10
Blackamber	0	96.6	3.4

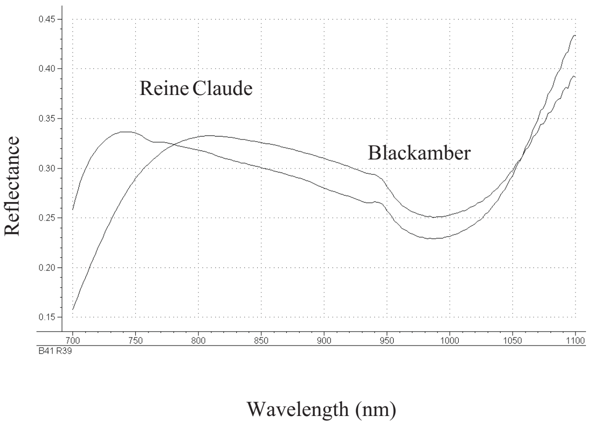

Fig. 4. Averaged reflectance spectra (MSC pre-processed) of plum samples having the same ratio of SSC and acidity.

It was found that the most important ranges of NIR, for classification between the groups having the same values of SSC/acidity, were 715-740 and 820-850 nm.

DISCUSSION

All plums were tested after being kept at room temperature (20°C) for 24 h for equilibration. They were of uniform maturity and surface features and ready consumption.

From chemical analysis, it was noticed that there was a wide diversity in the SSC of both plum varieties (CV average is about 20%), this diversity is also clear in Fig. 2. Moreover, the acidity in both varieties had a high variation (CV average is about 30%). This indicates that the samples were heterogeneous in terms of SSC and acidity aspects. Nevertheless, the classification was based on plum samples having the same values of SSC/acidity, which means that the effects of SSC and acidity were eliminated.

The MSC pre-processing technique was used for spectra data analysis. It was found that the full MSC pre-processing technique describes the data better than the raw data itself or first and second derivative pre-processing techniques, since the MSC yielded the lowest mean square root of error of prediction (RMSEP) rather than any of the other techniques. Moreover, distinct groups (two varieties) are explained very clearly along the first principal component (PC), see Figs 1 and 5. The MSC technique corrects the additive and multiplicative effects in the spectra and improves the predictive ability (Mobley *et al.,* 1996).

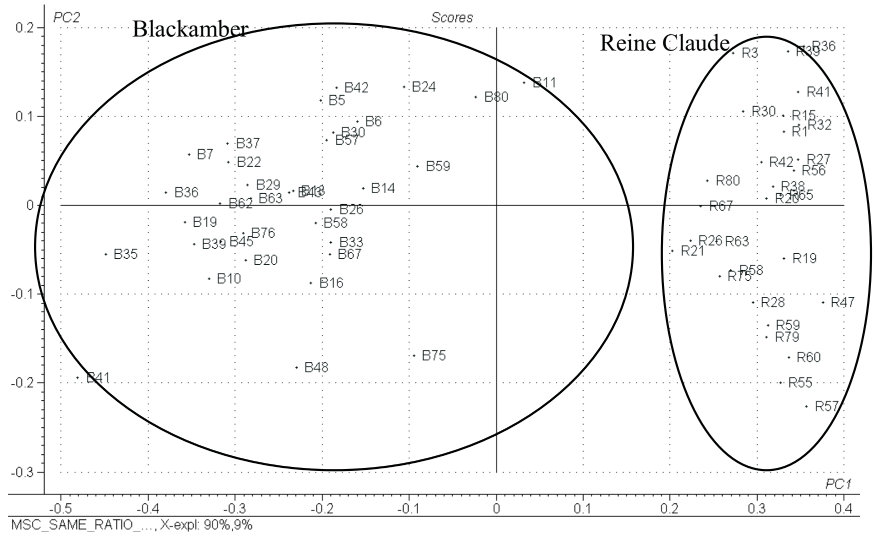

Fig. 5. Scores plot of the reflectance spectra of plum samples, which have the same ratio of SSC and acidity.

T a b l e 3. Classification result of NIR reflectance spectra for two plum varieties having the same values of SSC/acidity

Variety	Reine Claude	Blackamber	Error
	(%)		
Reine Claude	92.8	0	7.2
Blackamber	0	92.8	7.2

It was possible to model SSC, with a reasonable validation correlation coefficient of 80%. The most important range for modelling SSC was 778-810, 902-935 and 960-990 nm, since these ranges have the highest loading variables. It was difficult to model acidity. This may be due to the high variation and limited range in plum acidity. The failure of modelling acidity agrees with most research which states that it is not easy to model acidity in fruit.

The classification rate using the SIMCA technique was quite high. All plum samples were relatively highly classified, Reine Claude and Blackamber were correctly classified in 90 and 96.6% of the cases respectively at 5% significant level. This agrees with Fig. 3, which shows clearly separate groups in both varieties.

When considering classification of samples having the same values of SSC/acidity, both Reine Claude and Blackamber were correctly classified in 92.8% of the cases at 5% significant level. This agrees with Fig. 6, which shows clearly separate groups for both varieties. The wavelengths which have the highest discrimination power (in the 'Unscrambler' package, the variables which have a discrimination power greater than 3 are those which have the highest discrimination power) between plum samples having the same ratio of SSC and acidity are in the ranges of 715-740 and 820-850 nm. This indicates that the characteristic taste parameters which distinguish plums samples having the same ratio of SSC and acidity from both varieties, are in these ranges. More investigation of the chemicals in these ranges should be done.

The stability of the light source (halogen lamp) in the spectrometer was quite acceptable. The lamp was stable with a variation of less than 5% versus time and temperature during the whole period of reflectance measurements. The fruit was of uniform surface temperature after equilibration at 20^{o}C for 24 h.

In the reflectance spectra scores plot (Figs 1 and 5), the first principal component (latent variable), can be interpreted as a variety factor, since there are clearly separate groups (two varieties) along this vector.

In this research, it is believed that NIR senses characteristic taste parameters of plums, since the classification was based on plum samples having the same ratio of SSC and acidity and all the other parameters were equal, taste is the only remaining parameter that plum classification was based on.

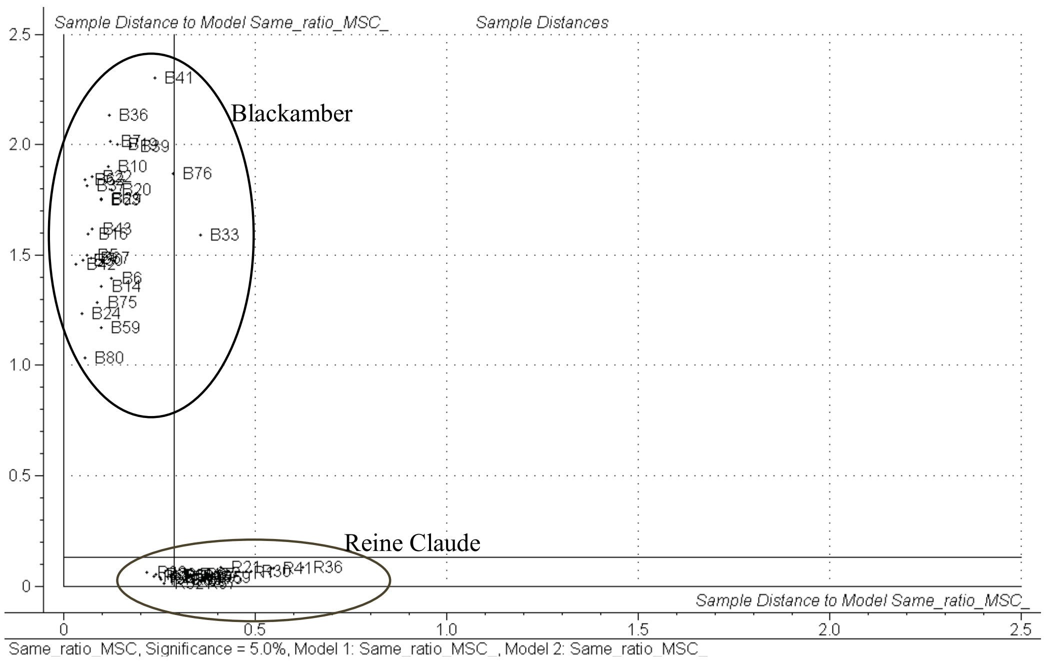

Fig. 6. Coomans plot for all Blackamber and Reine Claude samples which have the same ratio of SSC and acidity, at 5% significant level (Dark gray: train set, light gray: test set).

CONCLUSION

NIR was able to sense the overall taste of plums, including SSC and acidity (by classification between two varieties of plums). Moreover, NIR was able to sense the characteristics taste parameters of plum samples, (by classification between two varieties having the same ratio of SSC and acidity). This result is promising for studying taste parameters other than SSC and acidity using NIR technology.

Further work using NIR technology will be carried out at The Royal Veterinary and Agricultural University (KVL) on apples and tomatoes, to follow the development of taste components during ripening and to investigate more taste parameters.

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