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# NMR Spectrometers as "Magnetic Tongues": Prediction of Sensory Descriptors in Canned Tomatoes

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Supporting Information

**ABSTRACT:** The perception of odor and flavor of food is a complicated physiological and psychological process that cannot be explained by simple models. Quantitative descriptive analysis is a technique used to describe sensory features. Nevertheless, the availability of a number of instrumental techniques has opened up the possibility to calibrate the sensory perception. In this frame, we have tested the potentiality of nuclear magnetic resonance spectroscopy as a predictive tool to measure sensory descriptors. In particular, we have used an NMR metabolomic approach that allowed us to differentiate the analyzed samples based on their chemical composition. We were able to correlate the NMR metabolomic fingerprints recorded for canned tomato samples to the sensory descriptors bitterness, sweetness, sourness, saltiness, tomato and metal taste, redness, and density, suggesting that NMR might be a very useful tool for the characterization of sensory features of tomatoes.

**KEYWORDS:** NMR, multivariate analysis, sensory analysis, canned tomatoes

## INTRODUCTION

It is crucial to know consumers' expectations, habits, and preferences to ensure product success on the market. Brand, label information (such as geographic origin, technology, etc.), price, packaging, factory image, product concept, and effective communication are all critical factors. However, when the consumer decides whether to buy the product again or not, success is tightly connected to the products' features.

It is therefore extremely important to understand how much consumers' preferences are driven by differences in sensory features between products. Traditional consumer research helps determine acceptable versus unacceptable. It is helpful when an overall, synthetic understanding of the product's acceptance is needed. However, it is not of any help when an explanation, in terms of sensory descriptors, is needed to provide R&D with technical information useful to enhance product features. Such information can only be provided through analytical products evaluation, of which consumers are not capable.

A detailed sensory description, in fact, requires the ability to decompose each sensory feature, requires selective attention, and thus requires people specifically trained to the application of sensory analysis (quantitative descriptive analysis, QDA).[1] Sensory analysis is a discipline through which the sensory analyst evokes, measures, analyzes, and interprets human responses to stimuli as perceived through the senses. Human sensory tests are regularly employed in the food and beverages industries, and they are sometimes integrated by a number of techniques, including the electronic nose[2] and the electronic tongue.[2] The most common types of sensors used are based on electrochemical techniques, such as potentiometry and voltammetry.[3−5] Other sensing methods include optical[6] and acoustic techniques.[7] Furthermore, techniques like mass spectrometry (MS)[8] and gas chromatography (GC)[9] have also been used. $^1$H nuclear magnetic resonance (NMR) spectroscopy also has been used to investigate the taste of wine.[10] Here, we investigate the utility of $^1$H NMR as a tool to analyze the taste of canned tomato without any other chemical analysis.

## MATERIALS AND METHODS

**Materials.** Eighteen canned tomato products of different brands were purchased in different markets in the city of Napoli (Italy) (Table S1 in the Supporting Information).

**Sensory Assessment.** A panel of trained 12 assessors (six females and six males) was selected based on the ability to recognize, describe, and quantify basic tastes, odors, and texture properties. The panel developed a specific profile protocol for QDA containing 14 descriptors: redness, synaeresis, dimension, residual peel, consistency, density, tomato flavor, saltiness, sourness, bitterness, sweetness, tomato taste, cooked taste, and metal taste. Descriptors were evaluated on a continuous, unlabeled, 0−10 intensity scale and then turned into numeric variables

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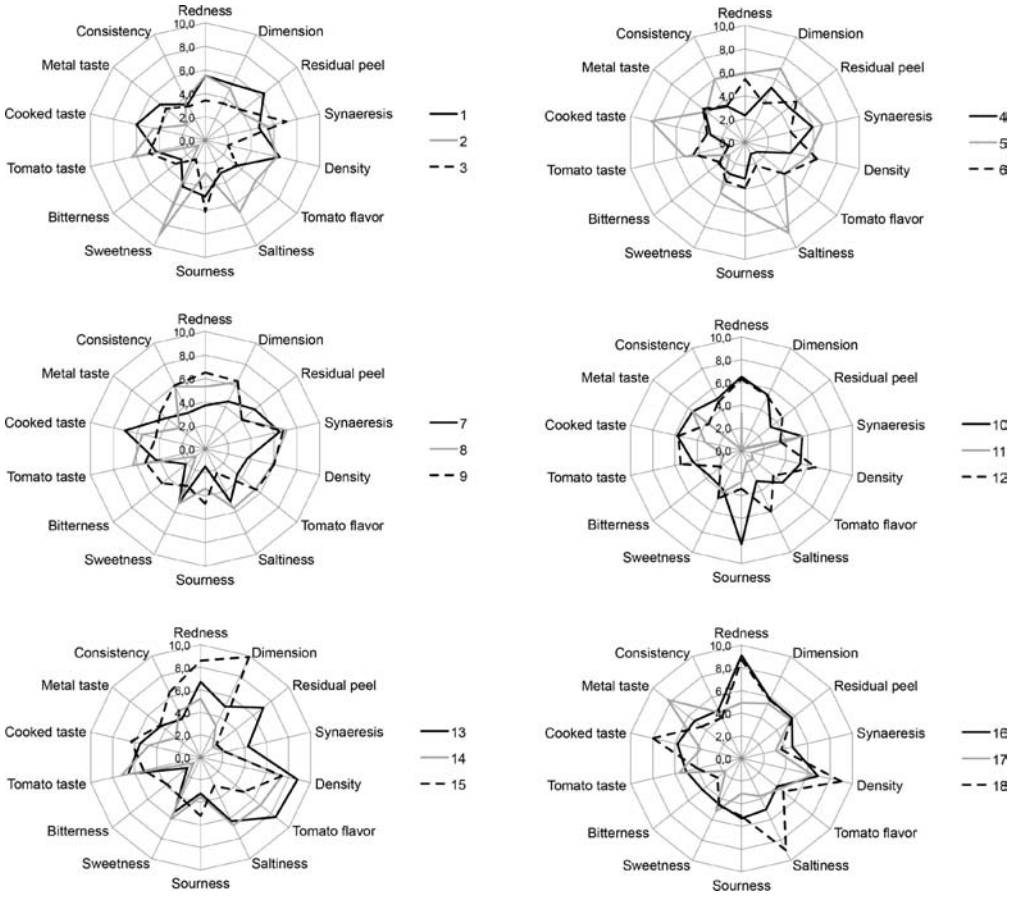


**Figure 1.** Spider web plot of the sensory descriptors for the 18 tested samples. The mean QDA parameters are listed in Table S2 in the Supporting Information.

(a number between 0 and 10). Three replicates per sample were performed, to minimize random errors (each subsequent replicate after 1 week from the previous one). The 18 samples were presented blinded in a flat plastic plate uncooked and at a controlled temperature (30 °C). A maximum of three samples were presented during each session according a balanced rotation plan.

**Sample Preparation for $^1$H NMR Analysis.** Each sample was blended and centrifuged at 2200*g* for 30 min. Four aliquots (500 $\mu$L) of supernatant of each sample was diluted with 100 $\mu$L of $D_2O$ and analyzed independently. No buffer was used.

**Chemicals and Reagents.** Deuterium oxide ($D_2O$, 99.9 atom %) was purchased from Cambridge Isotope Laboratories, Inc.

**NMR Spectrometry.** $^1$H NMR spectra were acquired at 25 °C with a 700 MHz Varian Unity Inova spectrometer using a 5 mm $^1H\{^{13}C/^{15}N\}$ triple resonance probe. The $^1$H NMR measurements were carried out with 128 transients and 16K complex data point. The recycle time was set to 5 s, and a 45° pulse angle was used. The water signal was suppressed using presaturation.

**NMR Data Reduction and Processing.** The spectra were processed using iNMR (www.inmr.net). An exponential line-broadening of 0.5 Hz was applied to the free-induction decay prior to Fourier transformation. All spectra were referenced relative to external sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS), phased, and baseline corrected. Four aliquots of each product were studied by one-dimensional $^1$H NMR. In total, 72 spectra were acquired. The spectra were aligned by correlation optimized warping[11] using $m_P = 50$ and $n_P = 2$. Data reduction was accomplished by dividing the spectrum into 0.01 ppm regions (bins) over which the signal was integrated to obtain the signal intensity. The region around the residual water signal (5.0−4.7 ppm) was removed in order not to compromise the analysis. The high- and low-field ends of the spectrum, containing no signal, were also removed (i.e., leaving data between 9.5 and 0.5 ppm). At the end, a total of 870 variables were analyzed for each spectrum. The integrals were normalized to a total intensity to suppress trivial separation based on variations in the amount of sample.

The dendrograms describing the sensory analysis were based on unscaled sensory data. The NMR-based dendrograms were based on PLS-DA scores of VAST scaled[12] NMR data calculated using Simca-P 11.5 (Umetrics, Umeå, Sweden) as input. In VAST scaling,[12] each region/bin is divided by the average standard deviation of the integral of that region within each product. This scaling reduces the weight of random variations between "identical" samples, and the analysis is not biased toward compounds present at high concentrations. The number of axes for the PLS-DA model was determined by leave one out cross-validation, where all of the samples from each of the 18 products were left out for one product at a time to determine the quality of the model. The model used was estimated using all 18 products. Hierarchical cluster analysis (HCA) was then carried out using complete linkages in *R* (http://www.r-project.org) by using the Euclidean distance between the PLS scores for each product.

Principal component analysis (PCA) was carried out on unscaled sensory data. VAST-scaled[12] NMR data were used. The PCA was performed using Simca-P 11.5 (Umetrics). The number of principal components (PCs) was determined by leave one out cross-validation as described above. To test which PCs that varied significantly between products, the PC scores for the NMR data were subjected to one-way analysis of variance using sequential Bonferroni correction for multiple testing (significance level, 0.05). The fact that the variations between the samples from the

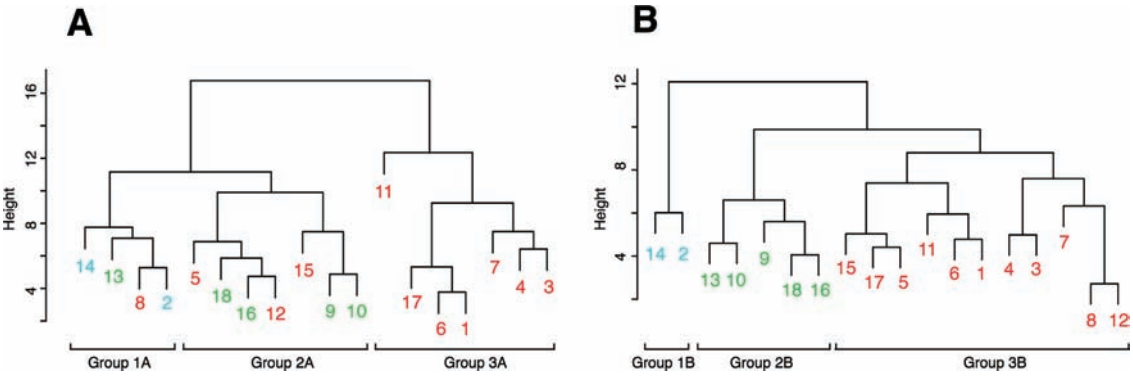


**Figure 2.** Dendrograms showing the similarities between products based on (A) QDA and (B) NMR. Products falling within the same group in the NMR classification are indicated with the same color.

same can were taken as the variation within the product might result in an overestimation of the significance. Standard errors (SEs) were calculated as $SE = SD/N^{1/2}$ where SD is the standard deviation and $N$ is the number of samples from that product.

Orthogonal projection to latent structures, OPLS, separates the variance in $x$ correlated with $y$ ($y$-predictive) with the orthogonal (noncorrelated; $y$-orthogonal) variance.[13] In contrast to regular PLS, a single $y$ will result in only one predictive component. OPLS was carried out using each sensory descriptor as the $y$-variable. Data were scaled to obtain unit variance and then centered. OPLS was performed using Simca-P 12.0 (Umetrics). Cross-validation was obtained as described above. Markers for the sensory descriptors were identified from the NMR signals that showed a strong correlation ($R^2 > 0.5$) with the OPLS predictive scores for the sensory descriptors.

## RESULTS AND DISCUSSION

**Sensory Analysis.** QDA mean results are reported in Figure 1. To group products sharing similar sensory features, HCA was performed on QDA means. The resulting dendrogram is shown in Figure 2A. Three main groups were identified, consisting of products 14, 13, 8, and 2 (group 1A); products 5, 18, 16, 12, 15, 9, and 10 (group 2A); and products 11, 17, 6, 1, 7, 4, and 3 (group 3A).

PCA was also performed on the same data set (Figure 3). Two PCs accounting for 60% of the variation were identified. A plot of their scores (Figure 3A) shows the positioning of the products according to their sensory attributes and allowed the identification of the most important sensory descriptors for products differentiation. This analysis indicates that the groups identified by the HCA share the same features and that there is no strong separation between the different groups identified. According to the loading plot (Figure 3B), the transition from the upper-left corner to the bottom-right corner of the map shows the simultaneous decrease of the bitterness and metal taste and increase of the sweetness and saltiness. Tomato flavor, saltiness, and tomato tastes are positioned on the bottom-right side of the map. Redness, consistency, dimension, density, residual peel, sourness, and cooked taste are positioned in the upper-right quadrant. In general, products belonging to group 1A are characterized by sweetness, by tomato taste and saltiness, and by tomato flavor. Group 2A is instead characterized by a more marked redness and sourness. On the other hand, group 3A is characterized by bitterness and metal taste, having a light

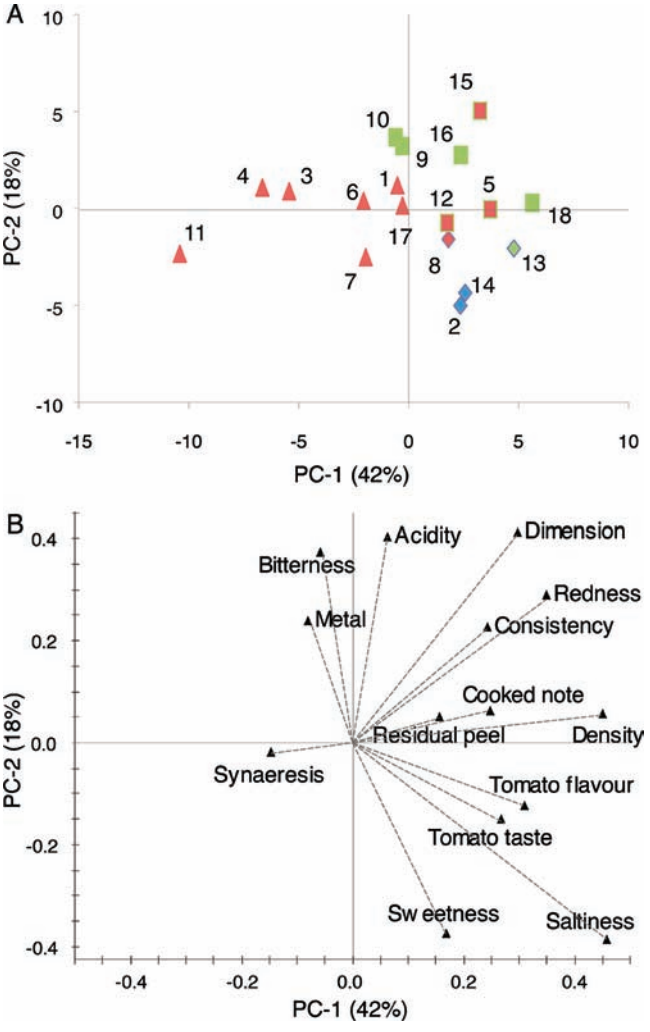


**Figure 3.** Score (A) and loading (B) plots of the PCA performed on sensory data. Products are colored according to NMR HCA analysis in Figure 2B. Note that none of the sensory descriptors are well described by this PCA model ($|R| > 0.5$ for all descriptors).

redness. However, none of the descriptors shows a high correlation ($|R| > 0.5$) with the model (Figure 3B).

To characterize the correlations between different sensory descriptors, the correlation coefficients were calculated (Table 1).

**Table 1. Correlation Coefficients ($|R| > 0.5$) between Sensory Descriptors[a]**

| | redness | dimension | synaeresis | density | tomato flavor | saltiness | sourness | sweetness | bitterness | tomato taste | cooked taste | consistency |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| redness | | 0.60 | | 0.76 | | | | | | | 0.56 | 0.55 |
| dimension | 0.60 | | | 0.55 | | | | | | | 0.51 | 0.87 |
| synaeresis | | | | −0.60 | | | | | | | | |
| density | 0.76 | 0.55 | −0.60 | | 0.71 | 0.57 | | | | 0.59 | | 0.56 |
| tomato flavor | | | | 0.71 | | 0.52 | | | | 0.86 | | |
| saltiness | | | | 0.57 | 0.52 | | | 0.58 | −0.52 | 0.57 | 0.71 | |
| sourness | | | | | | | | | 0.54 | | | |
| sweetness | | | | | | 0.58 | | | −0.69 | 0.52 | | |
| bitterness | | | | | | −0.52 | 0.54 | −0.69 | | | | |
| tomato taste | | | | 0.59 | 0.86 | 0.57 | | 0.52 | | | | 0.58 |
| cooked taste | 0.56 | 0.51 | | | | 0.71 | | | | | | |
| consistency | 0.55 | 0.87 | | 0.56 | | | | | | 0.58 | | |

[a] Sensory descriptors showing $|R| < 0.5$ to all other sensory descriptors are excluded.

We can see, for example, a strong negative correlation of sweetness with bitterness but not with metal taste or sourness, as suggested by the loadings plot (Figure 3B).

**NMR Analysis.** The same products tested in the QDA were analyzed by NMR. The superimposition of two representative $^1$H NMR spectra is reported in Figure 4. It should be noticed that for each product, all of the NMR samples were taken from the same can. The data might thus underestimate the spread of the chemical properties within each product. Analogously to the HCA performed on sensory data, the HCA analysis performed on the NMR data revealed three main groups (Figure 2B): 14 and 2 (group 1B); 13, 10, 9, 18, and 16 (group 2B); and 15, 17, 5, 11, 6, 1, 4, 3, 7, 8, and 12 (group 3B). Despite the fact that the two HCAs refer to data collected by very different analytical techniques, it can be seen that there is a good global agreement between the different measurements: All products of group 1B (products 2 and 14) are also present in group 1A, all products except one in group 2B (products 9, 10, 16, and 18) are also present in group 2A, and all products in group 3A (products 1, 4, 6, 7, 11, and 17) are also present in group 3B.

PCA has also been performed on the NMR data set. Fourteen PCs were identified, of which PC1, PC2, and PC3 vary significantly between the different products. These three PCs account for 57% of the variation. The general distribution of the products in the score plots (Figure 5A,B) in a way recall the one observed in the sensory data set (Figure 3A). For example, considering the PC1−PC2 plot, products 3 and 4 are mapped close to each other and, at the same time, far away from the products 9, 10, 16, 15, and 18. Similarly, these latter samples are far way from products 2 and 14. Finally, the products 1, 6, 7, 8, 12, and 17, which were placed in the very center of the plot of the sensory data (Figure 3A), are placed in the center of NMR PC1−PC2 plot as well. As judged from the loading plots (Figure 5C−E), the first PC describes the distribution of the samples based on their sweetness. In fact, negative values can be observed for signals belonging to sugars like saccharose and $\alpha$- and $\beta$-D-glucose. At the same time, positive correlations can be observed for signals belonging to bitter amino acids like tyrosine, phenylalanine, tryptophane, and isoleucine (see Chemical Signatures of Sensory Descriptors). The noisy look of the second PC describes the formation of sharper NMR signals due to a decrease in viscosity. The third PC seems instead related to an increase of saccharose, isoleucine, and acetate and a decrease of tyrosine, $\alpha$-D-glucose, malate, and glutamate.

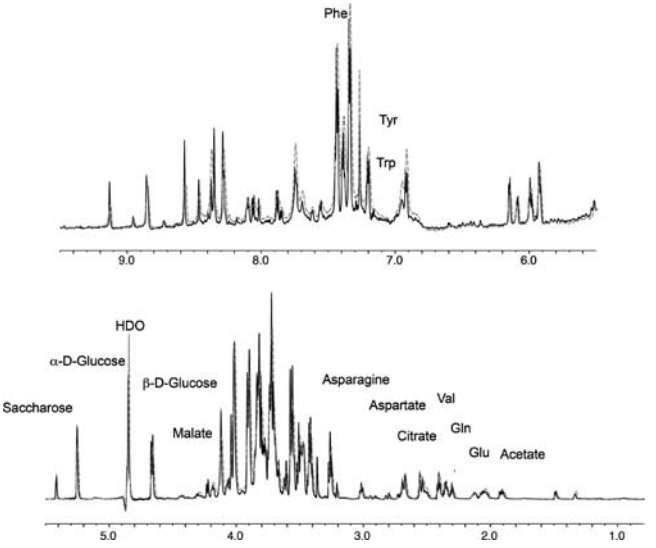


**Figure 4.** Annotated $^1$H NMR spectra of two typical canned tomato samples. Product **2** (solid black line) is characterized by the presence of saccharose (see signals at 5.41 ppm) and a low viscosity, while product **15** (dashed gray line) is characterized by the absence of saccharose and a high viscosity. Note that the *y*-axis scale of the upper panel is increased 40× compared to the lower.

The loading plots also contain a number of signals that could not be assigned unambiguously.

**Prediction of Sensory Descriptors.** Although it is encouraging that there are similarities in the structures of the sensory and NMR data, the important question is how well the sensory descriptors can be predicted by NMR. To resolve that question, we made predictive models for the different sensory descriptors using orthogonal-projection to latent structures, OPLS.[13] Using this protocol, we were able to get good predictions [$Q^2$(cum) > 0.5] for bitterness, redness, density, and metal and tomato taste (Table 2). After inspection of the remaining models and identification of outliers in those, we were able to get good models for all but two brands for saltiness, sweetness, and sourness (Table 2). In five cases out of six, the removed products showed extreme values for saltiness (2 of 2), sweetness (2 of 2), and sourness (1 of 2). It thus seems that these extra strong features depend on other factors than those under more normal conditions. The remaining

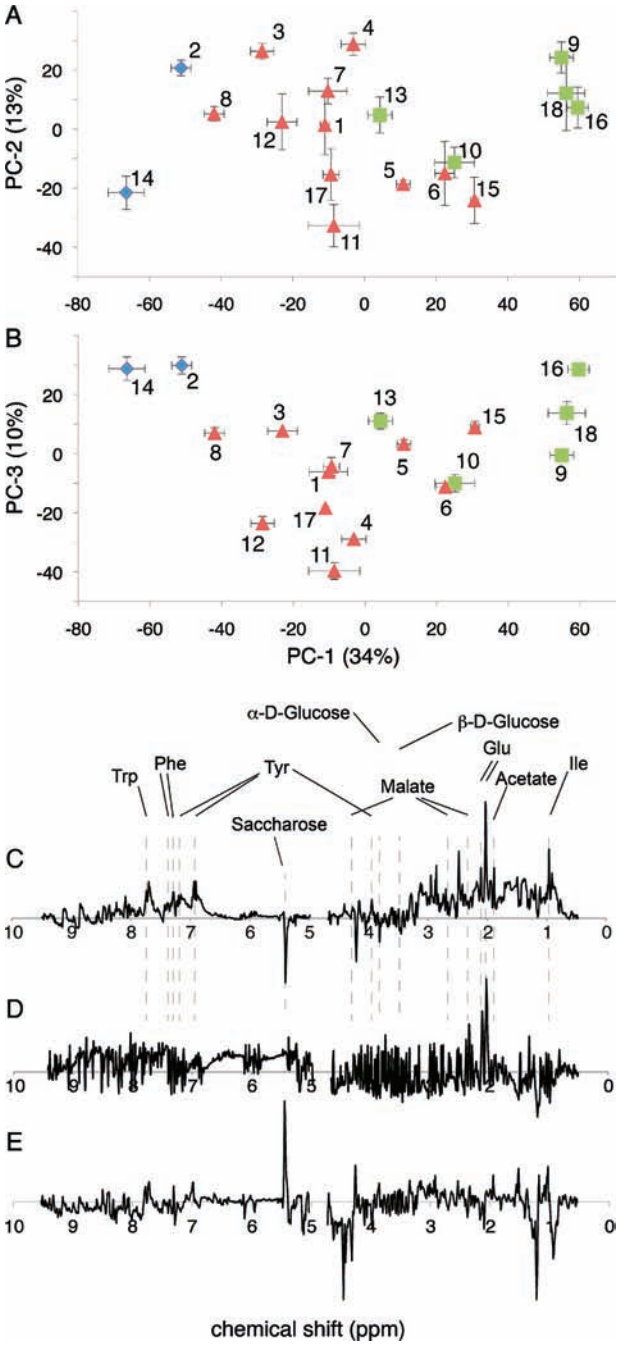


**Figure 5.** Score (A and B) and loading (C−E) plots of the PCA performed on NMR data. Panels A and B show the PC1−PC2 and PC1−PC3 score plots, and panels C−E show the PC1−PC3 loadings. Products are colored according to NMR HCA analysis in Figure 1B. Error bars correspond to one SE (SE = SD/$N^{1/2}$).

descriptors were related to the physical rather than chemical properties of the products.

**Chemical Signatures of Sensory Descriptors.** To determine the chemical components responsible for a given sensory descriptor, we have looked for all possible correlations between the NMR signals and the analyzed sensory descriptors using OPLS models. Specifically, the origin of signals displaying correlation above $R^2 > 0.5$ with the OPLS scores for the sensory descriptors with a $Q^2 > 0.5$ was identified. In this procedure, a multitude of

**Table 2. Description and Statistical Summary of the OPLS Models Constructed Based on NMR Data**

| variable | $A^a$ | $N^b$ | $R^2X$(cum)$^c$ | $R^2Y$(cum)$^c$ | $Q^2$(cum)$^d$ |
|---|---|---|---|---|---|
| bitterness | 7 | 66 | 0.70 | 0.99 | 0.87$^e$ |
| redness | 5 | 66 | 0.65 | 0.98 | 0.86$^e$ |
| density | 2 | 66 | 0.37 | 0.80 | 0.68$^e$ |
| metal taste | 1 | 66 | 0.31 | 0.85 | 0.67$^e$ |
| tomato taste | 2 | 66 | 0.42 | 0.87 | 0.58$^e$ |
| saltiness | 1 | 66 | 0.27 | 0.71 | 0.33 |
| *products 5 and 18 excluded* | *5* | *58* | *0.66* | *0.99* | *0.91*$^e$ |
| sweetness | 2 | 66 | 0.40 | 0.84 | 0.30 |
| *products 2 and 3 excluded* | *7* | *58* | *0.72* | *0.99* | *0.78*$^e$ |
| tomato flavor | 2 | 66 | 0.34 | 0.74 | 0.23 |
| residual peel | 1 | 66 | 0.30 | 0.56 | 0.14 |
| consistensy | 2 | 66 | 0.43 | 0.73 | 0.07 |
| | *2* | *62* | *0.37* | *0.79* | *0.26* |
| sourness | 0 | 66 | 0.23 | 0.31 | 0.04 |
| *products 3 and 10 excluded* | *5* | *58* | *0.65* | *0.96* | *0.83*$^e$ |
| syneraesis | 1 | 66 | 0.29 | 0.59 | 0.02 |
| dimension | 0 | 66 | 0.21 | 0.36 | 0.02 |
| cooked taste | 0 | 66 | 0.21 | 0.32 | −0.01 |

$^a$ A number of orthogonal components. $^b$ Number of samples included in the model. $^c$ $R^2X$(cum) and $R^2Y$(cum) = the cumulated fraction of the variance in the parameter explained by the model. $^d$ $Q^2Y$(cum) = the cumulative predicted fraction of the variation of the parameter as determined by cross-validation. $^e$ $Q^2Y$(cum) values above 0.5 are considered as good predictors.

chemical components were identified for several of the sensory descriptors[14] (see also Table 3).

It was possible to identify only very few compounds that have a relationship with sweetness. Particularly, sweet perception was positively correlated with saccharose (5.41 ppm) in spite of its low concentration, whereas it was negatively correlated with tyrosine (H-$\alpha$ 3.94 ppm), which is a known bitter amino acid. No correlation was found with citrate, while a negative correlation with the malate signal at 4.29 ppm was found. This is an interesting result since malate and citrate seem to have very similar sensory properties (see below).[15] The characteristic sweet−sour taste of tomato and its overall flavor intensity are mainly due to reducing sugars, free acids, and free amino acids, minerals, and volatile substances. Overall, the character and intensity of taste are greatly affected by the salts present and by the buffer effect of the various cations and anions. About 50% of the dry matter in tomatoes is made of sugars, primarily glucose and fructose. There is frequently saccharose as well, but its quantity rarely exceeds 0.1% of the fresh mass.[16,17] It is interesting to note that the sensation of sweetness cannot solely be explained by the sugar content. In fact, Jones and Scott did not find a close correlation between sugar content and sweetness.[18] Similarly, Watada and Aulenbach did not find correlation between sweetness and dry matter content either.[19] All of this means that other components affect the perceived sweetness. Interestingly, Stevens and co-workers found a relationship between the sensation of sweetness and the glucose/citric acid interaction.[20] Particularly, they have found that glucose affects sweetness more than fructose with high citric acid concentration. Furthermore, when the sugar concentration is low, citric acid reduces perceived sweetness, while with high sugar concentration, it increases sweet perception. It has been estimated that the relative composition in

**Table 3. Correlation between Chemical Substances and OPLS Models for Sensory Descriptors[a]**

| | redness | metal taste | saltiness | sourness | sweetness | bitterness | tomato taste |
|---|---|---|---|---|---|---|---|
| acetate (1.91) | | | | | | + | |
| aspartate (2.68, 2.80) | | | | + | | + | |
| asparagine (2.87, 2.95) | | | | + | | | |
| citrate (2.53, 2.66) | | | | + | | | |
| glucose (3.49, 3.82) | | − | | − | | − | |
| glutamate (2.05, 2.16, 2.32) | | | | + | | + | |
| glutamine (2.14, 2.45) | | | | + | | | |
| isoleucine (0.93, 1.26, 1.46, 1.98) | | + | − | + | | + | − |
| malate (2.37, 2.66, 4.29) | | + | − | + | − | + | − |
| phenylalanine (7.30, 7.40) | | + | | + | | + | |
| saccharose (5.41) | | − | | | + | − | |
| tryptophan (7.17, 7.29, 7.75) | + | | | + | | + | |
| tyrosine (3.94, 6.90, 7.18) | + | + | | + | − | + | |
| valine (2.53) | | | | + | | + | |

[a] + and − signs indicate positive and negative correlations, respectively. Chemical shift values (ppm) of the used signal are reported in brackets.

glucose, fructose, and citric acid can explain about 80% of the variation in sweetness.[20]

In contrast to sweetness, bitter taste was negatively correlated with glucose and saccharose signals and positively correlated with a number of bitter amino acids[21] like isoleucine (H-$\beta$, H-$\gamma$1, H-$\gamma$2, and Me-$\gamma$ at 1.98, 1.46, 1.26, and 0.93 ppm, respectively), tryptophan (H4, H5, and H6 at 7.75, 7.17, and 7.29 ppm, respectively), tyrosine (H3/H5 and H2/H6 at 6.90 and 7.18 ppm, respectively), valine (H-$\beta$ at 2.53 ppm), and phenylalanine (H3/H5 and H2/H6 at 7.40 and 7.30 ppm, respectively). The correlation with glucose suggests that even if glucose did not correlate with sweet taste, it has a strong masking effect on the bitter taste. Sweetness and bitterness show a relatively strong anticorrelation ($R = -0.69$; Table 2). Interestingly, bitter taste was also positively correlated with glutamate signals (H-$\beta$1, H-$\beta$2, and H-$\gamma$ at 2.52, 1.62, and 32 ppm, respectively), acetate (1.91 ppm), and malate (2.37 and 2.66 ppm), all compounds that do not possess a bitter taste themselves. However, the taste-enhancing effect of the glutamic acid, one of the most abundant amino acid in tomato, was proven,[22−24] and we cannot exclude a similar effect also for acetate and malate.

The sour taste of tomato can be ascribed mainly to the organic acids, rather than to the hydrogen ion concentration. Organic acids form more than 10% of the dry content of tomatoes.[25,26] The two main acidic components are citric and malic acid, where malic acid is more sour than citric acid even if present in lower concentration. In our case, we found that sourness is positively correlated with both of these components. Moreover, it is known that sourness is also affected by the presence of free amino acids.[27] We found positive correlations with amino acids having taste-enhancing properties like glutamate, glutamine, aspartate, and asparagine and with amino acids having a bitter taste like tryptophan, tyrosine, phenylalanine, valine, and isoleucine. Interestingly, sour taste was negatively correlated to the presence of $\alpha$- and $\beta$-D-glucose. All of these data strongly suggest that sour taste is closely correlated to bitter taste. As shown in Table 2, the correlation coefficient between the two was 0.54 in this study.

Furthermore, tomato taste and saltiness were all positively correlated (Table 2) and were negatively correlated to isoleucine (H-$\gamma$ and Me-$\gamma$ at 1.26 and 0.93 ppm, respectively) and malate (4.29 ppm). Metal taste, instead, had positive correlations with bitter amino acids like isoleucine (H$\gamma$ and Me$\gamma$ at 1.26 and 0.93 ppm, respectively), tyrosine (H3/H5 and H2/H6 at 6.90 and 7.18 ppm), and phenylalanine (H3/H5 and H2/H6 at 7.40 and 7.30 ppm, respectively). On the other hand, a negative correlation was evident with the signal belonging to $\alpha$- and $\beta$-D-glucose (3.82 and 3.49 ppm) and saccharose (5.41 ppm). Interestingly, metal taste was also positively correlated to the malate signal at 4.28 ppm. Metal taste did not show any correlations above $|R| = 0.5$ with other sensory descriptors in this study.

Very surprisingly, redness was positively correlated with the presence of tryptophan (H4, H5, and H6 at 7.75, 7.17, and 7.29 ppm, respectively) and tyrosine (H3/H5 at 6.90 and H-$\beta$s at 3.06 and 3.18 ppm). At this stage, we cannot explain this observation.

Finally, a number of signals in the region between 4.30 and 4.60 ppm and at 4.03 ppm display negative correlations with density. For the time being, we are not able to unambiguously assign these signals, even if their chemical shifts strongly suggest that they could be attributed to sugars.

In conclusion, the perception of odor and flavor of food is a complicated physiological and psychological process that cannot be explained by simple models. This is because hundreds of compounds simultaneously influence the human olfactory receptors and because the physiological response is far from linear, and the overall effects are not just the superimposition of the effect of single stimuli.

Sensory analysis, and, in particular, the QDA, continues to be an irreplaceable technique to describe sensory features. Nevertheless, the availability of a number of instrumental techniques has opened up the possibility to calibrate the sensory perception. Thus, the tandem approach that uses instrumental and classical sensory analysis seems to be a valuable strategy. Unfortunately, the more usual artificial tongue/nose are used to determine very specific components of the analyzed food. Furthermore, not all instrumental techniques are able to analyze directly the genuine mixture interacting with our sense without any extraction/concentration procedures. For example, MS and GC require volatilization of the analyzed compounds that very often is obtained with a chemical derivatization. In this frame, we have tried to test the potentiality of NMR spectroscopy as a predictive tool to measure sensory descriptors, without performing any complementary chemical analyses. In particular, we have used an NMR

metabolomic approach since it is rapid, sensitive, and relatively inexpensive. This approach in combination with multivariate analysis has an advantage over the ordinary sensory test, since it offers more reliable results for the classification and determination of some aspect of the sensory attribute of the tomato. The metabolomic fingerprints recorded for all tested canned tomato samples allowed us to differentiate all analyzed samples based on their chemical composition.

Interestingly, the same classification and characterization have been reached independently from the QDA analysis. In particular, a number of sensory descriptors can be easily predicted from the NMR data: bitterness, sweetness, sourness, saltiness, tomato and metal taste, redness, and density. The presence of a number of bitter amino acids like isoleucine, tryptophan, tyrosine, phenylalanine, and valine is correlated with bitterness and surprisingly to sourness. Other amino acids seem also to have a crucial role as taste enhancers like glutamate, glutamine, aspartate, and asparagine, which amplify the bitter and the sour taste, as well as the cooked taste. The sugar content is obviously correlated with sweetness, even if their correlation is not so straightforward. Finally, other components like citrate, malate, formiate, and acetate are correlated with sourness. Very interestingly, citrate and particularly malate seem to be crucial in the defining the taste of tomato. In general, we have noted that the same substances could be involved in two (or more) features; these could be counteractive in the sense that the increase in one leaves less room for the other features; they could be also affected by a third feature, etc. One drawback with the methodology presented here is that only the soluble fraction of the product is measured. In future studies, this can be avoided by using HR-MAS NMR where also the semisolid fractions contribute to the NMR spectrum. However, the results obtained suggest that NMR could be a very useful tool for the characterization of some sensory features of tomato. To evaluate the applicability of this methodology to other kinds of food, a number of experiments are currently undertaken in our laboratories.

## ■ ASSOCIATED CONTENT

**Supporting Information.** Tables of the identities of the canned tomatoes used in this study (Table S1) and of the QDA mean results forming the basis for Figure 1 (Table S2). This material is available free of charge via the Internet at http://pubs.acs.org.

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