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ARTICLE

Triple Concentrated Tomato Paste: Discrimination between Italian and Chinese Products

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^{1}H NMR spectroscopy was applied to discriminate triple concentrated tomato paste coming from two different countries. Notwithstanding different tomato cultivars and ripening stages employed to obtain the final product, significant discrimination between Italian and Chinese samples was obtained by combining NMR data and principal component analysis. Supervised orthogonal projection to latent structure discriminant analysis (OPLS-DA) technique was used to build robust classification models, while S-plot was employed to identify statistically significant variables responsible for class separation. Citrate content resulted in being the most relevant chemical compound for Chinese and Italian sample differentiation. In order to highlight other compounds able to contribute to sample differentiation, citrate content was excluded, and a new classification model was built. This latter model indicated aspartate, glutamine, and sugars as important variables in sample differentiation.

KEYWORDS: Triple concentrated tomato paste; OPLS-DA; S-plot; ^{1}H NMR; geographical origin

INTRODUCTION

Tomatoes (*Lycopersicum esculentum)* are one of the most important crops worldwide, either from an economical point of view or for their overall contribution to nutrition, being a good source of antioxidants such as carotenoids (lycopene and β-carotene) and polyphenols (flavonoids and hydroxy cinnamic acids). Tomatoes were largely farmed and processed with a production of 6 million tons and 33.6 million tons in Italy and China, respectively, during 2007 (www.faostat.fao.org). Processing tomatoes are largely viewed as an agricultural commodity used primarily as a foundation for more complex products. Tomatoes are consumed either fresh or as a range of processed products and have very distinct quality features; in particular, fresh ones must have acceptable flavor and handling characteristics to satisfy consumer demand and distribution requirements. However, processing tomatoes must have intrinsic rheological peculiarities, which make them suitable for the various processing applications such as juice, ketchup, or sauce production. Breeding companies have generated a range of tomato varieties aimed at satisfying all quality criteria; in addition, farmers are provided with germ plasma adapted to specific growing environments, thus allowing maximal scale and yield of production. Tomatoes are largely employed to obtain sauces, purées, and pastes (mono, double, or triple concentrated), and the processes behind these products are similar, unlike those involving pieces, such as diced tomatoes, pulp, or peeled tomatoes (*1*−*5*). The industrial processes are constituted by several steps: concentrated semifinished products are obtained from intact fruits, harvested without any particular selection for both ripening stage and cultivar, 15−20 cultivars are usually adopted, consistency being the main feature for the next processing step. The fruits are washed, enzymatically treated with a cold break inactivation (with temperature ranging from 65 °C up to 85 °C), peel and seeds are removed, and a multistep heat exchanger evaporation process up to about 38 °Brix content is performed at low temperature under vacuum. Aseptic filling, consisting of a thermal treatment (pasteurization) followed by a flash cooler in a plastic container of 220 up to 1000 kg/bags in a steel drum is finally carried out. Nowadays, food characterization is a very challenging topic because it includes both authenticity and geographical origin determination (*6*). Among all possible approaches, metabolomics has shown its great potentiality in the field of living systems, showing how the metabolic content is important for a comprehensive analysis of all metabolite changes upon stimuli (*7*). The metabolite content constitutes a sort of a fingerprint also for each single food product. Most of these studies have taken the advantage of the multivariate statistical approach to evaluate large sets of information obtained by advanced analytical techniques and to discriminate information dealing with redundancy often present in metabolomics data (*8*). The need for geographical characterization is of growing interest for consumers and producers during the last years, and several studies essentially based on isotopes, multielement analysis, or separation procedures (*9*−*14*) were applied to different foods.

Studies on tomato fruit appeared recently and were focused on the determination of maturity (*15*), on metabolite profiling (*16*, *17*) also in genetically modified ones (*18*), and on metabolic changes taking place upon fruit development and ripening (*19*−*21*). Very few studies were devoted to tomato juice

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(*22*−*24*) and to tomato paste (*25*, *26*). Finally, as far as we know, no data is present in the literature concerning the geographical origin determination of tomato fruits or tomato paste.

Despite an extensive market for imported triple concentrated tomato paste, coming in the last years from developing countries and mainly from the biggest tomato producer, China, there are very few indications about the possibility of identifying the origin and the quality of different tomato products (*15*, *27*). Triple concentrated tomato paste from China is cheaper than any others on the market even though, from a technological point of view, the equipment available in China is very updated, coming for the most part from Italy, considered worldwide as the best producer of tomato processing equipment. The request for an efficient analytical method comes from the necessity of several countries to declare the origin of the products used. In the last years, NMR techniques have demonstrated the high capability in food quality determination as well as in the geographical one. Its capability to obtain with a single experiment the quantitative evaluation of a large number of soluble compounds makes it a leading technique. Several NMR studies appeared in the literature applied to different foods: in our recent works, we obtained the geographical discrimination of honey and Parmigiano Reggiano by combining NMR data and multivariate statistical analysis (*28*, *29*). In this article, we investigated a possible geographical discrimination of triple concentrated tomato paste samples coming from different regions of China and Italy.

MATERIALS AND METHODS

NMR Analysis. Forty seven samples of triple concentrated tomato paste, 26 Chinese, and 21 Italian samples sampled from 220 kg aseptic bags were used. All samples were checked against standard parameters used for the quality assessment of these products (°Brix, total and volatile acidity, color, lactate, pH, consistency, and molds), and they all resulted within the standard values. Chinese samples were from different northwestern regions of China (Xinjiang, Tianjin, Gansu, and inner Mongolia), while Italian samples were from the main producers of both the north and south regions of Italy. Each sample for ^{1}H NMR analysis was obtained by dissolving 150 mg of lyophilized sample into 1 mL of deuterated water buffered with sodium diphosphate (600 mM) at pH 6.5; the solution was centrifugated at 13400 rpm for 10 min, and 0.6 mL of the supernatant was used for the NMR analysis. ^{1}H NMR spectra have been recorded on a Bruker DMX 500 spectrometer (Bruker Biospin GmbH Rheinstetten, Karlsruhe, Germany) operating at 11.7 T and equipped with a 5-mm reverse probe with z-gradient. All spectra were recorded at 300 K, with 6000 Hz spectral width and 65536 k of data points. Solvent suppression was achieved by applying a presaturation scheme with low-power radio-frequency irradiation. No resolution enhancement functions were applied before Fourier transformation; phase and baseline were automatically corrected with ACD/Spec Manager (ACD Laboratories, version 11, Toronto, Canada) software. Two-dimensional ^{1}H−^{1}H total correlation spectroscopy (TOCSY), ^{1}H−^{13}C heterocorrelated experiments such as heteronuclear single quantum coherence (HSQC) and heteronuclear multiple bond correlation (HMBC) were acquired for spectral assignment and identification of specific metabolites. Spectra were referenced and scaled to trimethylsilyl [2,2,3,3-^{2}H$_4$] propionate (TSP) external standard at 0.00 ppm for both proton and carbon dimensions, while spectra alignment for bucket integration was performed by using the α-glucose signal at 5.12 ppm. Spectra were reduced to integrated regions (buckets) of equal width (0.04 ppm) over the spectral region 10.40−0.08 ppm, excluding the residual water region between 4.72 and 4.88 ppm.

Statistical Methods. NMR data were imported into SIMCA-P+ 12 (Umetrics, Umea, Sweden) for statistical data analysis. Principal component analysis (PCA) and orthogonal projection to latent structures discriminant analysis (OPLS-DA) were performed with mean centering as data pretreatment. The OPLS technique is an extension of the supervised PLS regression method (*30*) that produces models of clearer interpretation. In this respect, OPLS removes the so-called structured-noise from a given data set and decomposes the factor data matrix X into two blocks corresponding to the variations correlated and noncorrelated to the response Y. As well as PLS, OPLS can be used for discrimination analysis by introducing dummy variables. The main benefit resides in the ability of OPLS-DA to collect information in predictive latent variables reducing the model complexity. This advantage is magnified when the two classes model is investigated. In this latter case, only one component is needed to explain the variation between the two classes, while the analogue PLS-DA model could produce more than one component. Furthermore, when only one latent variable is able to model the response, the predictive score vector t can be directly used to highlight resonances acting as potential markers. This purpose could be easily achieved by building the S-plot (*31*) obtained by plotting the loadings

$$p_i = \frac{x_i^t t}{t^t t}$$

proportional to the covariance between the variable x_i and the predictive score vector t against

$$p(\mathrm{corr})_i = p_i \left(\frac{t^t t}{x_i^t x_i} \right)^{1/2}$$

corresponding to the correlation coefficient between x_i and t. The calculated $p(\mathrm{corr})_i$ can be considered as a measure of the similarity between the t score and the x_i variable, while the loading p_i represents a measure of the variation of the variable x_i along the t score. Since the t score is the best variable fixed by the model to separate the classes, a potential marker must show a high absolute p(corr) value and loading.

T2 and distance to the model (DModX) tests were applied to verify the presence of outliers and to evaluate whether a submitted sample falls within the model applicability domain. The commonly adopted statistical molecular design method called D-optimal onion design (*32*) was applied to select both training and test sets. Unlike other statistical methods (*33*, *34*), onion design merges several D-optimal designs in concentric layers, thus resulting in an optimized minimal set of selected observations with maximal diversity. By using MODDE 8.0 (Umetrics, Umea, Sweden), training and test sets, containing 28 and 19 samples, respectively, were extracted from the observation space described by using PCA scores.

RESULTS AND DISCUSSION

The complete ^{1}H NMR spectrum and expansion of the aromatic region of triple concentrated tomato paste are represented in **Figure 1A**. Assignment of resonances were performed and confirmed on both the basis of previous assignments (*23*) and upon addition of standard compounds. Small chemical shift differences (ca. 0.1 ppm) with previously published results may be due to different sample concentrations. The aliphatic region of the ^{1}H NMR spectrum is dominated by the presence of monosaccarides, such as glucose and fructose, while amino and organic acids were revealed in less extent. In particular, in the aliphatic region of the spectrum, methyl-amino acids such as Ile and Val, amino acids such as Glu, Asp, Gln, and Asn were easily recognized. Other organic acids, such as malate, lactate, and γ-aminobutyrrate were also assigned. Particularly interesting is the doublet centered at 2.43 and 2.59 ppm due to the proton resonances of citrate: its larger line width with respect to all other NMR signals suggested the presence of a fast exchange between free and metal ion−citrate complex, thus resulting in a line broadening of the resonance, as already suggested and proved in a previous paper (*23*).

Concerning sugar resonances, the anomeric protons of both α and β glucose were easily identified, at 5.12 and 4.53 ppm, respectively; the use of TOCSY, in combination with the HSQC spectrum, allowed the identification of all resonances for both isomeric forms of glucose. Fructose resonances were also

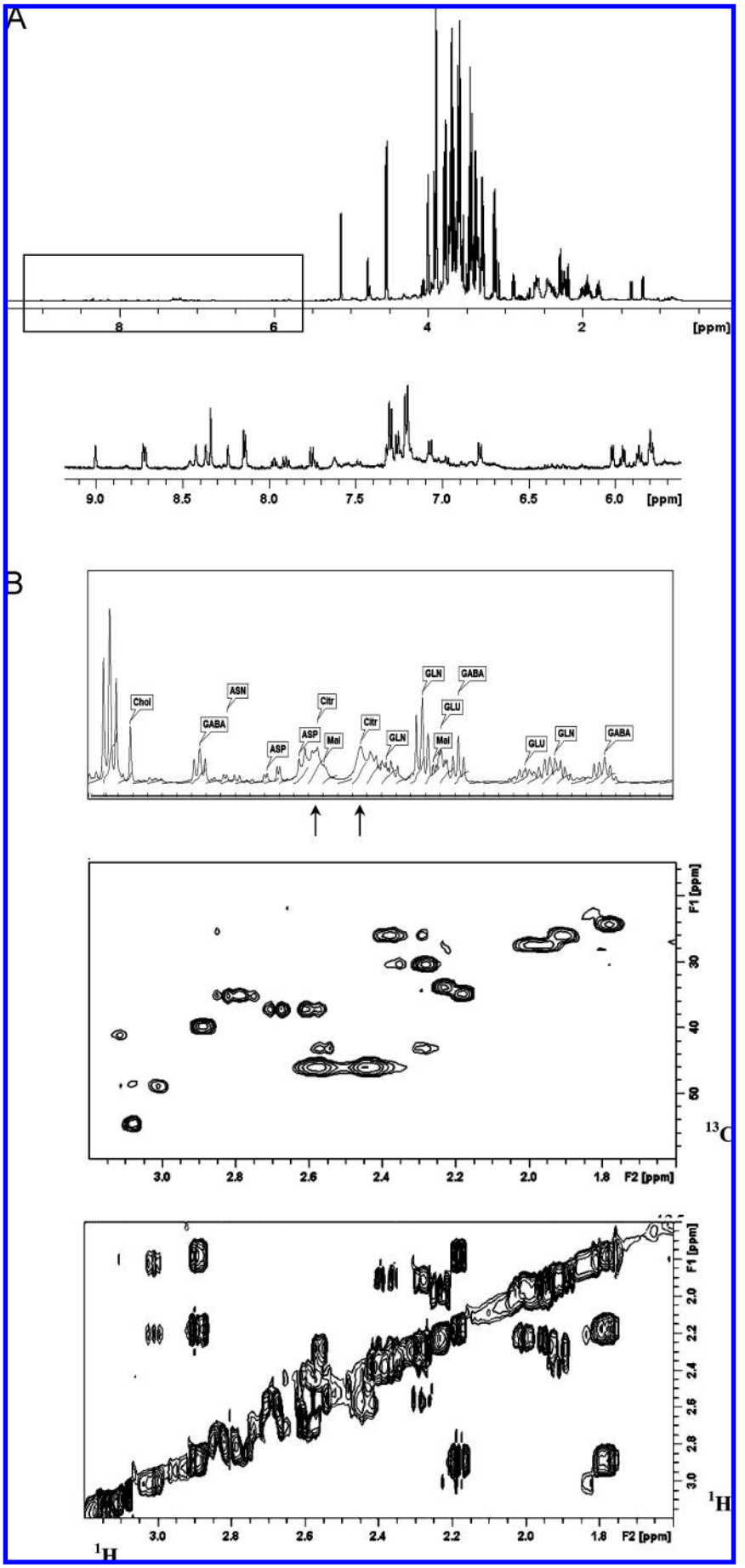

Figure 1. (**A**) ^{1}H NMR spectrum of a triple concentrated tomato paste sample lyophilized and dissolved in water. Expansion of the aromatic region is also shown. (**B**) Expansion of TOCSY and HSQC spectra corresponding to the aliphatic region with assigned resonances. Buckets involving citrate resonances, omitted in the second OPLS-DA model, are indicated by arrows.

Table 1. Resonance Assignments of Triple Concentrated Tomato Paste Sample Metabolites in Water Solution[a]

	chemical shifts					
	H_α	H_β	others	C_α	C_β	others
Ala	3.67	1.36		51.2	16.8	
Asn	3.9	2.77/2.84		51.7	35.1	
Asp	3.78	2.59/2.69		52.7	37.2	
Gaba	2.18	1.78	2.89	34.8	24.2	39.8
Gln	4.06	1.91/2.28	2.38	58.9	25.9	30.4
Glu	3.65	2.00/1.94	2.24	55.1	27.4	33.9
Ile	3.49	1.85	1.34/1.13/0.89/0.82	nd	nd	15.0/22.3
Phe			7.29/7.26/7.21			129.7/128.5/130.1
Thr	4.15	3.49	1.22	66.3	61.0	20.5
Tyr			7.07/6.78			131.5/116.5
Val	3.5	2.14	0.92;0.87	nd	nd	18.0
citrate			2.43;2.59			46.0
choline			3.08			54.6
ethanol			3.55/1.07			nd
formate			8.34			nd
lactate			4.02/1.22			68.6/20.4
malate			4.16/2.56;2.29			70.9/43.2
αGlu			5.12/3.43/3.605/3.30/3.71/3.71;3.66			92.8/72.1/73.3/70.2/72.1/61.2
βGlu			4.53/3.137/3.38/3.29/3.38/ 3.78;3.61			96.5/74.8/76.4/70.2/76.4/61.4
αFruF			3.54;3.48/-/4.00/3.88/3.95/3.72;3.61			63.2/104.9/82.5/76.6/82.0/61.2
βFruF			3.49;3.45/-/4.00/4.00/3.72/3.68;3.54			63.4/102.0/75.5/75.5/81.3/63.4
βFruP			3.60;3.45/-/3.68/3.78/3.89/3.91;3.60			64.3/98.6/68.1/70.2/69.8/64
trigonelline			9.00/8.73/8.71/7.97/4.22			146.2/147.0/128.1/50.0
AMP			8.34/8.15/6.02/4.67			140.9/153.3/87.5/74.2

[a] $^1H/^{13}C$ chemical shifts are reported on the basis of TOCSY, HSQC, and HMBC experiments.

identified: in particular, the overlapped resonances at 4.00 ppm, revealed distinct ^{13}C chemical shifts corresponding to $C_3\alpha FF$ and $C_{3,4}\beta FF$, while the combined use of TOCSY, HSQC, and HMBC allowed identification of the two furanosidic α and β isoforms of fructose. The β piranosidic fructose isoform (βFP) was identified on the basis of standard fructose solution acquired in water.

The aromatic region indicated the presence of two predominant aromatic amino acids (Tyr and Phe) and in very low concentration other aromatic compounds such as trigonelline and nucleotides, as previously determined (*24*); compounds such as flavanones are known to be accumulated in tomato peel, and for this reason were not detected here (*17*). Lycopene was not detected as well because of its water insolubility; as a matter of fact, it was detected in tomato juice (*22*) only after extraction with organic solvents. The combined use of TOCSY and HSQC spectra (**Figure 1B**) led to the assignment of the most relevant compounds observed in the water solution of triple concentrated tomato paste, shown in **Table 1**.

^1H NMR spectra were subjected to bucketing with a chosen bucket size of 0.04 ppm. This value was selected as the optimal compromise between selectivity and signal shifts present even though buffered solutions were employed and applied to all ^1H NMR spectra. Preliminary PCA analysis with mean centering as data pretreatment was performed on all samples. Four components explained 79.6% of the total variance (R^2), with the prediction goodness parameter $Q^2 = 0.56\%$. In this model, only one sample resulted in a strong outlier by considering the T2 test; nevertheless, this sample was not excluded by further analysis. The score plot of the first two PC's highlighted the clear sample separation (**Figure 2**) already present simply by using the unsupervised PCA model.

These model scores were used to represent the space of the observations, sampled with D-optimal onion design, thus obtaining a balanced training and test sets constituted by 28 samples (39% Italian and 61% Chinese) and 19 samples (53% Italian and 47% Chinese), respectively. The training set was used to perform

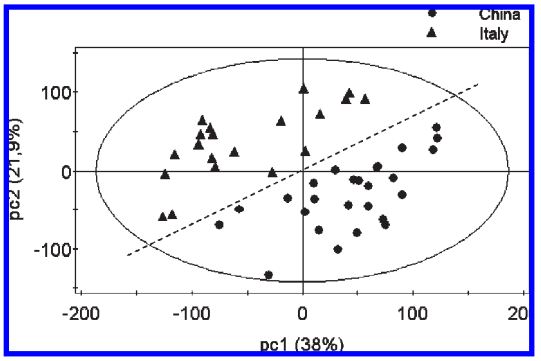

Figure 2. PCA score plot performed by considering all 47 triple concentrated tomato paste samples: filled triangles and dots represent Italian and Chinese samples, respectively. Pc1 = 38.0%, and pc2 = 21.9%. R^2 = 79.6% e, and Q^2 = 56.0%.

an OPLS-DA model with two classes (Italian and Chinese samples): this model showed one orthogonal component, with $R^2 = 0.85$ and $Q^2 = 0.78$. On the basis of T2 and DModX tests (data not shown), the model created was suitable for the prediction of the geographical origin of both training and test set samples. All samples were correctly predicted as could be evaluated by the classification list, shown in **Table 2**. Each training sample was classified by means of a classification score (Y calculated) indicative of its representativeness. In our case, all samples were correctly classified, by using 0.4 and 0.6 as thresholds for classification, thus indicating a good model.

A particularly useful tool that compares the variable magnitude against its reliability is the S-plot obtained by the OPLS-DA model and represented in **Figure 3A**. It showed the most relevant variables aimed to sample differentiation between the two classes: in particular, buckets at 2.43 and 2.55 ppm were the most characterizing for the Chinese samples. A more clear representation can be observed in **Figure 3B** and **C**, where these two bucket values were represented for all of the NMR spectra. **Figure 3B**

Table 2. Classification List for 28 Triple Concentrated Tomato Paste Samples Constituting the Training Set and 19 Triple Concentrated Tomato Paste Samples Constituting the Test Set Re-Projected onto the OPLS-DA Model Performed by Considering All Spectra Buckets (Left) and by Excluding 2.43 and 2.55 Citrate Buckets (Right)[a]

training				test			
OPLS-DA		OPLS-DA without citrate		OPLS-DA		OPLS-DA without citrate	
samples	Y calculated	samples	Y calculated	samples	Y predicted	samples	Y predicted
I1	**0.95**	**I1**	**0.89**	**I2**	**0.96**	**I3**	**0.91**
I3	**1.02**	**I2**	**0.93**	**I7**	**0.97**	**I4**	**0.78**
I4	**0.81**	**I5**	**0.76**	**I8**	**0.98**	**I8**	**1.07**
I5	**0.83**	**I6**	**0.83**	**I9**	**1.02**	**I11**	**1.09**
I6	**0.8**	**I7**	**1.02**	**I11**	**1.03**	**I13**	**1.03**
I10	**1.15**	**I9**	**1.04**	**I14**	**0.73**	**I16**	**0.53**
I12	**1.14**	**I10**	**1.16**	**I15**	**0.95**	**I18**	**0.94**
I13	**0.9**	**I12**	**1.18**	**I16**	**0.67**	**I21**	**0.82**
I19	**0.95**	**I14**	**0.59**	**I17**	**0.91**	C2	−0.11
I20	**0.76**	**I15**	**1.02**	**I18**	**0.91**	C12	−0.02
I21	**0.72**	**I17**	**0.92**	C7	−0.11	C13	0.04
C1	0.19	**I19**	**0.94**	C8	−0.21	C14	0.31
C2	−0.11	**I20**	**0.81**	C12	0.07	C15	0.15
C3	0.15	C1	0.15	C14	0.29	C18	−0.14
C4	0.07	C3	0.16	C15	0.17	C19	0.07
C5	−0.1	C4	0.18	C16	0.26	C20	0.10
C6	0.20	C5	0.02	C19	−0.01	C21	0.45
C9	0.13	C6	0.18	C20	0.17	C24	−0.18
C10	0.36	C7	−0.02	C26	0.1	C25	0.07
C11	0.32	C8	−0.03				
C13	0.10	C9	0.03				
C17	−0.04	C10	0.36				
C18	−0.3	C11	0.38				
C21	0.30	C16	0.10				
C22	−0.31	C17	−0.29				
C23	0.01	C22	−0.18				
C24	−0.09	C23	−0.03				
C25	0.11	C26	−0.08				

[a] I and C stand for Italian and Chinese samples, respectively.

indicated undoubtedly that the bucket between 2.43 and 2.47 ppm (half component of citrate at higher field) is sufficient to discriminate Italian from Chinese samples. The bucket between 2.55 and 2.59 ppm (half component of citrate at lower field, overlapped with Asp resonances) was also very critical for sample separation, although not so clear-cut as the previous one did (**Figure 3C**). Italian samples instead, appeared to be strongly characterized by a group of buckets such as 3.75, 3.67, 3.59, 3.35, 3.27, and 3.15 responsible for glucose and fructose resonances. Analysis of the S-plot revealed that beside citrate buckets, the other two buckets, at 2.59−2.63 and 2.39−2.43 ppm due to Asp and Gln resonances, respectively, are arising as characteristics for Chinese samples, even in lower amounts with respect to the previously mentioned buckets.

Our results demonstrated that simply on the basis of citrate content triple concentrated tomato paste samples can be differentiated according to their geographical origin. In particular, Chinese samples resulted in being much more enriched in citrate than Italian ones. On the basis of this model, all of the 19 test set samples were reprojected onto the OPLS-DA model, properly classified as shown in the classification list of **Table 2** (Y predicted).

As a matter of fact, it is well known that citrate can be added for pH correction and to avoid bacteria growth but are not allowed in these products. In this respect, a geographical discrimination between Chinese and Italian tomato paste based only on this variable could be biased by this compound. Therefore, new training and test sets were extracted by excluding 2.43−2.47 and 2.55−2.59 ppm buckets from the data set, with the use of the D-optimal onion design technique and the PCA scores to represent the sample space: 28 samples (46% Italian and 54% Chinese) and 19 samples (42% Italian and 58% Chinese) for training and test sets, respectively, were selected, being the same amount as in the previous model. New OPLS-DA with two classes (Italian and Chinese samples) were performed on the new training set resulting in 2 orthogonal components with $R^2 = 0.87$ and with $Q^2 = 0.77$. Also in this case, T2 and DModX tests (data not shown) were checked, and the model created was suitable for the prediction of the geographical origin of both training and test set samples. The new model revealed other buckets responsible for sample discrimination: in particular, buckets at 3.79 and 2.59 due to Asp and at 2.39 due to Gln characterized the Chinese samples. Italian samples resulted again characterized by larger amounts of both glucose and fructose content.

The classification list obtained for the new training and test sets shown in **Table 2** revealed that all samples were correctly predicted. However, three samples resulted as borderline in prediction, while they were correctly predicted by using 0.5 as the threshold level.

In contrast with other studies appearing in the literature focused on fresh tomato fruits, in the present study triple concentrated tomato paste, coming from different regions of China and Italy ready for reprocessing, was investigated. It is well known that ripening plays an important role in metabolite content differentiation because of the regulation of different metabolic pathways, as well as that expected from different varieties (*35*). An accurate selection is normally carried out on tomato products when the fruit itself is present in the finished

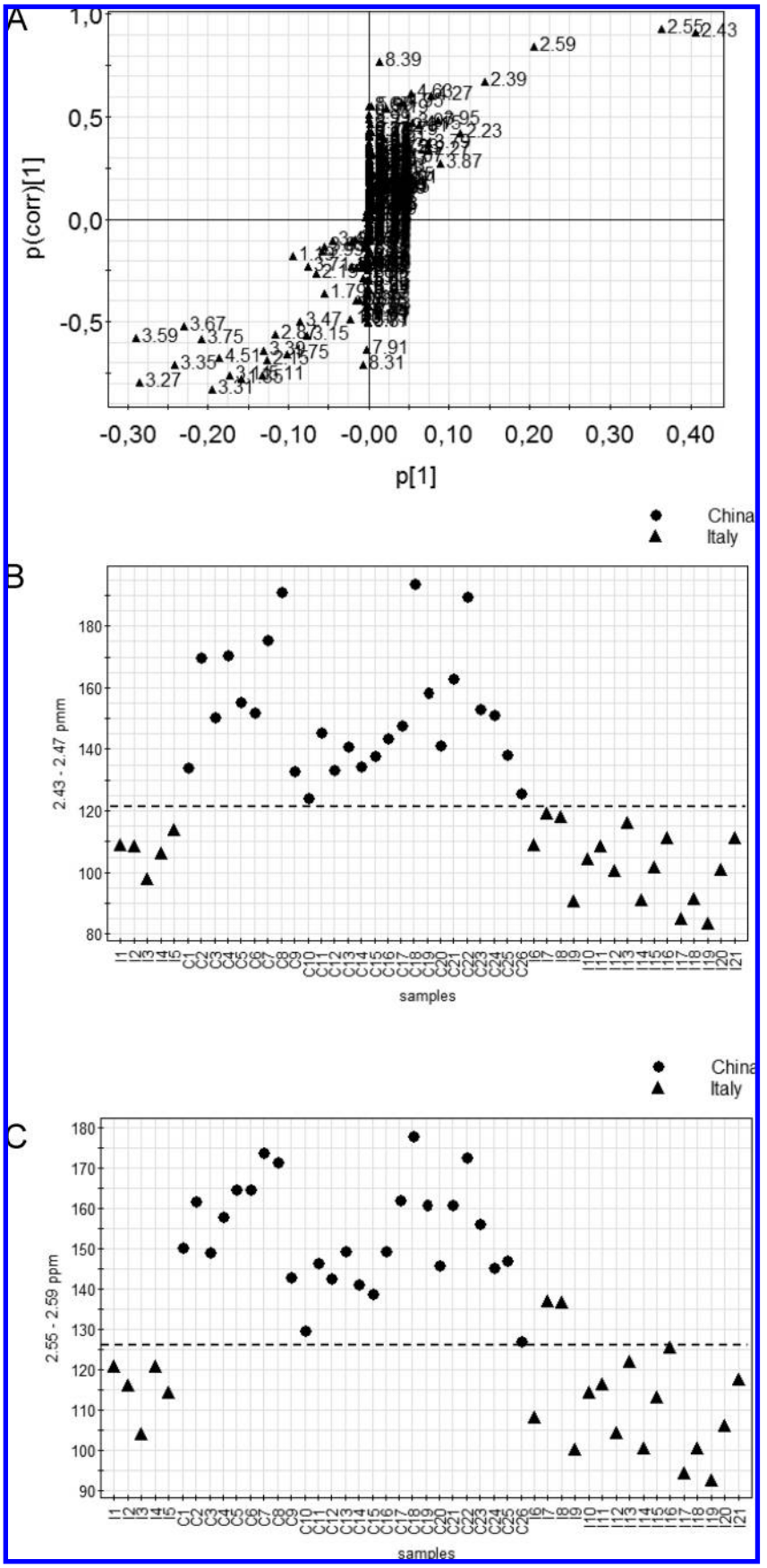

Figure 3. (**A**) OPLS-DA S-plot: variables 2.43 and 2.55 appeared to act as geographical markers. (**B** and **C**) Distribution of variable/bucket 2.43−2.47 (citrate, **B**) and 2.55−2.59 ppm (citrate, malate, and aspartate, **C**) among all triple concentrated tomato paste samples. Filled triangles and dots represent Italian and Chinese samples, respectively. Dotted lines indicate integral thresholds for sample separations.

product with pieces, such as diced, pulp, peeled, and so forth. On the contrary, triple concentrated tomato paste products, as previously discussed, are constituted by several cultivars at different ripening stages pooled to make the finished product, thus including all possible differences in metabolic profiles, that were mediated. In this respect, differences among cultivars, ripening stages, and all other possible factors affecting the metabolic content of these products cannot be used as variables to discriminate triple concentrated tomato paste by a statistical approach, and differences in the samples should then account only for the geographical origin.

Further evidence of this conclusion is made by the use of standard parameters for quality assessment of these products since they did not produce any sample differentiation in multivariate statistical analysis. In this respect, one of the possible reasons for such samples differentiation could be the different pedoclimatic conditions between Italy and China tomato farming. The comparison of the metabolite content obtained by the combined use of high resolution ^{1}H NMR and PCA analysis already revealed a feasible sample differentiation. Training and test sets selected by D-optimal onion design were used to build and to validate the OPLS-DA models. The model obtained considering all variables indicated that citrate content was the main component for sample differentiation and showed the capability to correctly predict the test set constituted by 19 samples of both Chinese and Italian origins. By excluding the contribution of citrate, present in larger amount in Chinese samples, a new OPLS-DA model indicated that sample origin differentiation based on Asp, Gln, glucose, and fructose content could still be possible. Italian samples resulted in both models being enriched in sugar content. Our results suggested the possibility of a clear distinction between Chinese and Italian triple concentrated tomato paste by means of ^{1}H NMR spectroscopy in combination with multivariate statistical data analysis. Furthermore, NMR confirmed its usefulness in food characterization: the importance of detecting several compounds with a single experiment was crucial for sample differentiation. A possible quality assessment of these geographically different triple concentrated tomato paste samples, in our opinion, has to be evaluated by further studies, enlarging the number of samples and by considering different growing season products as well as differences in process installations.

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