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Volatile Compounds, Polyphenols and Sensory Quality in the Production of Tomato Vinegar

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Abstract Fresh tomato and tomato products are widely consumed products. Their beneficial properties are not only present in fresh products but also in fermented ones. Therefore, the production of fresh tomato derivatives could be a good alternative to get a higher diversification and to make a good use of possible overproductions. Tomato vinegar from tomato paste by submerged culture fermentation has been developed. Final assays of maceration with rehydrated tomato paste (3, 5 and 7% v/v) in order to improve the final composition and organoleptic characteristics were also carried out. Polyphenols and volatile compounds have been determined along production and maceration processes. The statistical study (analysis of variance and principal component analysis) showed significant differences in volatile compounds and polyphenols according to matrix (rehydrated tomato paste, tomato wine and tomato vinegar) and specific maceration conditions (amount of rehydrated tomato paste and maceration time), which were also supported by sensory analysis. On the basis of the analytical and sensory results, 3 days of maceration and 5% v/v of rehydrated tomato paste were fixed as optimum conditions to obtain a tomato vinegar from tomato paste.

Keywords: *polyphenols, sensory analysis, tomato paste, vinegar, volatile compounds*

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1. Introduction

In the last few years, consumers are becoming more conscious of their nutrition and food health. In that way, the consumption of products with beneficial properties such as antioxidant, anti-inflammatory or anti-cardiovascular, and prevent certain diseases, has been on the rise.

Fresh tomato and tomato products such as sauces, purees and juices, are widely consumed products, particularly in Mediterranean countries because they are essential products of the healthy Mediterranean diet [1].

Among their beneficial properties; reduce cardiovascular, carcinogenic and degenerative diseases owing to the antioxidant capacity of vitamin C and their polyphenol content [2], prevent from obesity and diabetes [1] and they are a source of β-carotene, vitamin A and minerals [3].

These properties are not only present in fresh products but also in fermented ones, and therefore fermentation seems to be an ideal processing step: it increases the level of safety, extends shelf life and improves organoleptic properties [4,5].

Tomato exportations to countries beyond Europe, such as USA or Asian countries, has a problem when dealing with the fresh product but not with a non-perishable product [6]. The development of products from pre-processed raw materials, such as paste or tomato puree, facilitates not only the transport of the raw material to the destination country, but also the product homogeneity and availability of the product throughout years [6].

Commercially, two types of tomato paste can be found [7]. They differ in the degree of polygalacturonase and pectin methylesterase deactivation by heat treatment [7]. The first one, the "Hot-break" paste is obtained after a heat treatment of 90°C which completely deactivates the enzymes. Thus, pectin is not degraded and the product has a high consistency after rehydration [6]. The other paste, "Cold-break" one, is submitted to a minor heat treatment (60 to 70°C), so that the enzymes are partially denatured and, therefore, there is less concentration of pectins, giving a lower consistency to the final product [6]. This less aggressive heat treatment also results in obtaining a better colour and flavour in the final rehydrated product [7].

The fact that the high amounts of wine, and subsequent derived products such as vinegar, are being developed in many regions of the world, provides an opportunity for value-added product development through innovative formulas and technologies. In fact, nowadays, oenology market is turning towards diversification by means of the development of original, novel and enriched new products. Although Asian countries have a consolidate industry about these kind of products, a few researches about wine vinegars have been developed in Western countries. For instance, new Sherry vinegar derived products based on

maceration with different fruits [8], as well as fruit juices from different raw materials enriched with Sherry wine vinegar [9] have been developed. Regarding this, the oenological market, particularly vinegar market, has been diversified significantly in recent years, and products like fruit and vegetable vinegars are beginning to be investigated [10,11]. In fact, consumers are now starting to appreciate the healthy benefits of consuming vinegar, so there is a growing demand in markets for fruit vinegars that are sold as healthy foods [12], which could justify the development of a tomato vinegar.

Furthermore, the production of industrial vinegar (submerged culture) over traditional vinegar (surface culture) is more reliable for large scale production, because it is less susceptible to microbial contamination and it is faster due to the oxygen supply.

In addition, it works in a semi-continuous way which decreases production costs. That is the reason why this process methodology is replacing the traditional production of vinegar in some industries [13].

Taking all these facts into account, tomato vinegar by submerged culture from tomato paste as raw material has been developed and characterized in terms of volatile and polyphenolic compounds and sensory analysis.

2. Materials and Methods

2.1. Raw Material

A cold-break tomato paste (28/30ºBrix) supplied by Las Marismas de Lebrija, S.C.A. (Lebrija, Sevilla, Spain) was reconstituted following manufacturer´s instructions.

After rehydration, this raw material had an initial ºBrix around 5, which was insufficient to obtain vinegar with a proper acidity. Therefore, the matrix was sweetened up to 20 ºBrix adding sucrose in two steps: in the first one, 80 g/L of sucrose were added (up to 12ºBrix), and after alcoholic fermentation had started, other extra 80 g/L were added. The procedure was carried out in triplicate.

2.2. Wine Making

Laboratory scale alcoholic fermentations using 3L-glass vessels were carried out in triplicate. 60 mg/L of total sulphur dioxide (potassium metabisulphite, Agrovin, Spain) as antimicrobial agent, 3 mL/L of pectolytic enzymes (Enartis Zym RS, Trecate, Italy) as clarifying agent and 0.35 g/L of diammonium phosphate as nutrient were added to the matrix. The fermentation process was performed by inoculating 0.20 g/L of *Saccharomyces bayanus* active dry yeast (Enartis Ferm SB, Trecate, Italy) into the rehydrated tomato paste. It was previously activated at 35°C for 20 min. This process was controlled by measuring the sugar content. It was stopped when its value was around 1ºBrix. Then, the samples were centrifuged at 15000 g for 10 min and stored at 4 ºC.

2.3. Vinegar Making

2.3.1. Preparation of the Starting Culture

400 mL of unfiltered Sherry vinegar was centrifuged at 15000 g for 5 min to obtain the acetic acid bacteria starting culture. The obtained pellet, which contained acetic acid bacteria, was dissolved in 400 mL of tomato wine and it was divided into three 250 mL-flasks in order to multiply acetic acid bacteria by surface culture.

2.3.2. Acetic Fermentation

Acetification process was carried out, in triplicate, into an 8 L-Acetator Frings (Heinrich Frings, Bonn, Germany) by submerged culture. The measurement of alcohol content, which defined the loading/downloading conditions during the process, was performed by a calibrated alcohol sensor (Alkosens, Heinrich Frings, Bonn, Germany). When the alcohol percentage in the matrix was 0.3%, the downloading phase of vinegar started from 6 L to 2 L. Then, the loading phase of the wine started up to 6 L at low speed (5 mL/min) in order to avoid sharp changes in the alcohol content of the medium. An aeration flow of 7.5 L/hL was employed. The temperature was fixed at 29°C. 0.35 g/L of diammonium phosphate (Panreac, Barcelona, Spain) was added to guarantee the growing of acetic acid bacteria.

All the procedure was controlled by a computer program (Acetomat S7, Siemens AG, Munich, Germany).

2.4. Maceration Conditions

An assay of maceration of the final vinegars with rehydrated tomato paste was carried out in order to improve their organoleptic characteristics. Vinegar samples with 6 g acetic acid/100 mL were macerated for 0, 1, 3 and 7 days [14] (maceration time) at room temperature with different amounts of rehydrated tomato paste (3, 5 and 7% v/v). Samples were regularly homogenized during this process. All maceration studies were performed in duplicate.

2.5. Characterization of Samples

Volatile and polyphenolic compounds were analysed along the production process: initial (rehydrated tomato paste), after alcoholic fermentation (tomato wine), after acetic fermentation (tomato vinegar) and after different periods of maceration (0, 1, 3, and 7 days) with different amounts of rehydrated tomato paste (3, 5 and 7% v/v).

2.5.1. Analysis of Volatile Compounds

Volatile compounds were analyzed according to the stir bar sorptive extraction-gas chromatography-mass (SBSE-GC-MS) method proposed by Durán-Guerrero et al. [15]. For identification purposes, MS determination of commercial standards (Sigma, Steinheim, Germany) was performed and, retention indices for all the studied compounds were determined on a DB-Wax polar column and compared with those from literature (data not known).

For quantification, calibration curves with four levels of concentrations using commercial standards were done. All solutions were prepared in synthetic vinegar with 6 g acetic acid/100 mL. All analyses were done in duplicate.

2.5.2. Analysis of Phenolic and Furanic Compounds

All the samples were previously filtered through 0.45 and 0.22 µm nylon filters from Scharlab (Barcelona, Spain). The separation and identification of phenolic and furanic compounds were performed on a Waters Acquity

ultra pressure liquid chromatography (UPLC) system (Waters Corps. Milford, MA, USA), equipped with a diode array detector (DAD) following the method proposed by Schwarz et al. [16].

The identification and quantification of compounds were done using DAD chromatograms obtained at 280 nm (for gallic acid, 5-hydroxy-methyl-furfural, ρ-hydroxy benzoic acid, and tyrosol) and 320 nm (for caftaric acid, chlorogenic acid, caffeic acid, p-coumaric acid, ferulic acid, quercetin derivate, and quercetin-3-glucoside) by comparing retention times and ultraviolet-visible (UV-VIS) spectra with those provided from commercial standards (Fluka, Buchs, Switzerland; Sigma, Steinheim, Germany; and East Kodak, Rochester, USA).

Each compound was quantified by comparison with a calibration curve obtained with the corresponding standard at four levels of concentration, except caftaric acid that was quantified as caffeic acid and quercetin derivate that was quantified as quercetin. For this, different amounts of commercial standards were diluted in synthetic vinegar with 6 g of acetic acid/100 mL.

All analyses were done in duplicate.

2.6. Sensory Analysis

Vinegar samples after acetic fermentation and maceration study were submitted to sensory analysis. Assessment took place in a standard testing room [17], equipped with separated booths and olive oil testing glasses [18] in order to avoid the influence of the vinegar sample color. As well, glasses were covered with a watch-glass to minimize the escape of volatile substances. The room temperature was set at 22°C.

Eighteen trained judges, from personnel of laboratory, participated regularly in the tasting panel. The repeatability of their judgments was tested and confirmed for this kind of oenological samples.

20 mL of each sample was presented to the judges. Glasses were encoded with 3-digit numbers with key identification to facilitate collection and treatment of data.

A preference ranking test was used to evaluate the variability of samples. The olfactory impression of acetic acid content (8.5, 6 and 4 g acetic acid/100 mL) and tomato descriptor (addition of 3, 5 and 7% of rehydrated tomato paste (v/v) for 0, 1, 3 and 7 days of maceration) were evaluated by orthonasal way in duplicate.

2.7. Statistical Analysis

Analysis of variance (ANOVA), and component principal analysis (PCA) using the statistical computer packages Statgraphics Centurion, version 15.0 (Statpoint Inc., USA) for Windows XP were performed.

Sensory data were analyzed by using a spreadsheet (Microsoft Office Excel 2007). In this case, Friedman´s test was considered.

3. Results and Discussion

3.1. Alcoholic and Acetic Fermentations

Some routine analytical parameters correspond to rehydrated tomato paste, tomato wine and tomato vinegar are presented in Table 1. Alcoholic fermentation was over 4 days after inoculation, and 9.42% mean alcoholic content (v/v) was achieved. For obtaining tomato vinegar by submerged culture, 24 h were needed to complete a single load/download cycle. Mean values of 0.3% alcohol (v/v) and 8.75 g acetic acid/100 mL were achieved.

Table 1. Mean values and standard deviations for some routine analytical parameters

Parameter	Rehydrated tomato paste	Tomato wine	Tomato vinegar
º Brix	10.87±1.10	0.00±0.01	-
Titratable Acidity*	3.1±0.5	5.3 ±1.2	10.9±1.2
pH	4.50±0.04	3.83±0.05	3.08±0.11
Density	1.0431±0.0320	0.9780±0.0121	-
Alcoholic degree**	-	9.42±0.51	0.31±0.10

* (g/L tartaric acid)
** (% v/v).

3.1.1. Volatile Compounds

A total of 23 volatile compounds, belonging to different families, were identified and quantified in the three matrices considered (rehydrated tomato paste, tomato wine and tomato vinegar (Table 2).

Volatile data were submitted to analysis of variance (ANOVA). The independent factor considered was matrix (rehydrated tomato paste, tomato wine, and tomato vinegar). Tukey's test was used in the study of comparison of means.

As can be expected, most of volatile compounds showed significant differences according to matrix ($P < 0.05$). In general, alcoholic fermentation increased significantly the concentration of all volatile compounds, whereas the process of acetic fermentation reduced the content of all of them. Z-citral, E-citral, and 6-methyl-5-hepten-2-one, showed decrements along all production process. These volatile compounds were found in fresh tomato by Buttery et al. [19] who observed great decreases in several volatile compounds and increases in concentrations of linalool, 6-methyl-5-hepten-2-one and α-terpineol from fresh tomato to tomato paste. Viljanen et al. [20] found that high temperatures combined with either ambient or high-pressure decreased the levels of a lot of volatile compounds present in fresh tomato.

In relation to alcoholic fermentation, in grape wines, most esters are formed mainly through this process by yeasts [21]. Ethyl octanoate, ethyl decanoate and ethyl hexanoate were the major esters found in tomato wine obtained from fresh tomatoes [22]. In the present study, these ethyl esters together with isoamyl acetate, 2-phenylethyl acetate, ethyl-9-decenoate and ethyl isovalerate exhibited significant increases after alcoholic fermentation.

About acetic fermentation, the concentrations found for most volatile compounds decreased from tomato wine to tomato vinegar. These results agree with those obtained by Morales et al. [13], in studies of submerged acetification of Sherry wines. Significant losses of volatile compounds were observed due to the use of an open acetification system similar to the system used in our work.

As well as this fact, during the acetification process, the acetic acid bacteria can metabolise other alcohols in a

similar way to ethanol and produce their respective fatty acids [23]. It could explain the decreases in isoamyl alcohol and 1-octanol, and the increases in nonanoic acid and hexanoic acid found after acetic fermentation.

3.1.2. Phenolic and Furanic Compounds

Data were also submitted to analysis of variance (ANOVA) considering matrix as independent factor (rehydrated tomato paste, tomato wine, and tomato vinegar (Table 2). Tukey's test was used in the study of comparison of means. As can be seen (Table 2) the factor matrix was significant for most of compounds, with significant differences for tomato paste and tomato wine (Tukey´s test). Similar polyphenolic and furanic composition was found for tomato wines and tomato vinegars. Chlorogenic acid was the main hydroxycinnamic acid derivate found in tomato juices by Vallverdu et al. [2]. Tomato juices were also rich in caffeic acid, ferulic acid, ρ-coumaric acid and their glycosilated forms. Stewart et al. [24] reported that levels of quercetin in tomato juices ranging from 28 to 37 mg/L. Its content in tomato juice depends on fruit cultivar, country of origin, harvesting seasons and growing conditions [2].

A cold break tomato paste has been employed in this study. Its production process included a thermal treatment at temperatures between 60 and 70 °C and not addition of cream rich in peels and seeds. This peel contains several flavonoids of which naringenin, chalcone and rutin (quercetin-3-O-rutinoside) are predominant [25].

No addition of cream to cold paste and the lower solubility of polyphenols in an aqueous medium could explain the lower phenolic content found for rehydrated tomato paste obtained just after reconstitution. After alcoholic fermentation, samples showed significant increases in the content of most polyphenols and furanic compounds. 5-hydroxy-methylfurfural, ρ-hydroxy-benzoic acid, tyrosol, caffeic acid, p-coumaric acid, ferulic acid and quercetin-3-glucoside were only detected in fermentation products (Table 2). Tyrosol is produced from tyrosine by yeast during fermentation [26], therefore its increase after alcoholic fermentation is logical.

Table 2. Mean concentrations (μg/L, n=6) and standard deviations (SD) of the studied volatile, polyphenolic and furanic compounds.

Volatile compounds	Matrices					
	Rehydrated tomato paste		Tomato wine		Tomato vinegar	
	Mean	SD	Mean	SD	Mean	SD
Ethyl isovalerate	0.44^{b}	0.05	0.83^{a}	0.11	0.71^{ab}	0.09
Z-Citral	4.60	1.01	2.76	0.21	0.48	0.06
E-Citral	27.2^{a}	8.0	0.86^{b}	0.18	0.31^{b}	0.01
Isovaleric acid**	0.38^{b}	1.13	2.86^{a}	0.13	4.48^{a}	1.49
Decanal*	2.60^{ab}	0.21	4.52^{a}	1.09	1.56^{b}	0.46
α-Terpineol	5.01^{b}	1.76	10.40^{a}	1.36	6.08^{ab}	0.70
D-Limonene	110.1	10.1	90.4	9.1	84.8	10.2
Isoamyl acetate**	0.05^{b}	0.02	2.68^{a}	0.30	0.59^{b}	0.15
Isoamyl alcohol**	3.27^{c}	1.00	138.43^{a}	7.50	73.92^{b}	3.48
Ethyl hexanoate	2.37^{b}	1.03	452.7^{a}	25.2	6.86^{b}	2.20
6-Methyl-5-hepten-2-one	237.8^{a}	50.1	17.8^{b}	4.2	2.04^{b}	0.19
Nonanal	2.18^{ab}	0.38	4.94^{a}	1.01	n.d.^{b}	-
Ethyl octanoate	16.9^{b}	3.9	1262.8^{a}	77.3	44.9^{b}	12.5
Linalool	5.94^{ab}	1.00	7.94^{a}	1.55	2.05^{b}	0.34
1-Octanol	1.66^{b}	0.10	17.7^{a}	1.0	2.37^{b}	0.20
Ethyl decanoate	10.7^{b}	0.4	509.7^{a}	51.0	19.4^{b}	3.8
Ethyl 9-decenoate*	8.42^{b}	0.12	87.9^{a}	19.3	8.12^{b}	0.11
2-Phenylethyl acetate**	0.004^{c}	0.001	2.24^{a}	0.07	1.71^{b}	0.24
Hexanoic acid**	0.013^{c}	0.005	1.77^{b}	0.17	2.93^{a}	0.28
2- Phenylethanol**	0.027^{b}	0.010	21.6^{a}	0.6	20.3^{a}	0.20
Octanoic acid**	0.002^{c}	0.001	2.27^{a}	0.10	1.52^{b}	0.08
Nonanoic acid	0.40^{c}	0.07	2.57^{b}	0.06	4.56^{a}	0.04
Decanoic acid	0.14^{c}	0.02	10.5^{a}	0.51	2.17^{b}	0.16
Phenolic and furanic compounds						
Gallic acid**	n.d.^{a}	-	n.d^{a}	-	10.42^{b}	1.33
5-hydroxy-Methylfurfural**	n.d.^{a}	-	1.52^{b}	0.23	1.43^{b}	0.11
Caftaric acid**	3.30^{a}	0.37	2.67^{b}	0.36	2.11^{b}	0.24
p-hydroxy-Benzoic acid**	n.d.^{a}	-	2.26^{b}	0.40	2.76^{b}	0.32
Tyrosol**	n.d.^{a}	-	12.54^{b}	1.63	13.49^{b}	2.13
Chlorogenic acid**	10.21^{a}	0.31	7.50^{b}	0.26	6.40^{c}	0.88
Caffeic acid**	n.d.^{a}	-	3.65^{b}	0.18	3.96^{b}	0.55
p-Coumaric acid**	n.d.^{a}	-	0.57^{b}	0.13	0.84^{c}	0.26
Ferulic acid**	n.d.^{a}	-	0.62^{b}	0.09	0.64^{b}	0.13
Quercetin derivative**	19.24^{a}	0.95	63.89^{b}	6.33	60.11^{b}	9.78
Quercetin-3-glucoside**	n.d.^{a}	-	265.13^{b}	8.14	183.49^{c}	26.84

*Decanal, quantified by nonanal calibration curve; *Ethyl 9-decenoate, quantified by ethyl decanoate calibration curve; **: mg/L; n.d.: Not detected. Significant differences for the same row are indicated with different superscripts ($P < 0.05$).

Gil-Muñoz et al. [27] observed that during the alcoholic fermentation of Monastrell musts, the extraction of gallic acid, protocatechuic acid, ρ-hydroxybenzoic acid, vanillic acid, m-hydroxybenzoic acid and syringic acid depended on the ethanol content.

Darias-Martín et al. [26] found that during alcoholic fermentation a higher contact with solid parts produced wines with higher phenol values.

In the case of tomato wines, Owusu et al. [28] observed that the transformation of tomato fruits into tomato wines provoked an increase in the total polyphenolic content making that polyphenols were more soluble and biologically available compared with the fruit where they are tightly bound to others compounds.

In this study, it could be established that an increase of content in alcohol in the medium together with the use of pectolytic enzymes produced a higher solubilisation of this type of compounds [29].

3.1.3. Sensory Analysis

A preliminary sensory study revealed that the 8.5 g acetic acid/100 mL samples were excessively aggressive. On the other hand, samples without addition of rehydrated tomato paste were not appreciated (data not shown). So that, these two factors, acetic acid content and addition of different amounts of rehydrated tomato paste were studied from a sensory point of view. Firstly, two acetic degree values, 4% and 6% (w/v) were considered.

The statistical value of calculated F coefficient of Friedman (F_{cal}=11.89) was higher than the obtained for the critical value from Friedman Table (F_{tab}=10.88; 18 judges, 6 samples and 5% of error). This revealed significant differences among samples.

According to results, the best olfactory rating corresponded to the highest acetic acid content (61), being significantly better than the lowest score (41). Consequently this acetic degree value (6 g acetic acid/100 mL) was fixed for future studies.

3.2. Maceration Study

3.2.1. Volatile Compounds

In this case, volatile data were also submitted to analysis of variance. The independent factors considered were maceration time (0, 1, 3, and 7 days) and amount of rehydrated tomato paste (3%, 5%, and 7% v/v). Tukey's test was also used in the study of comparison of means.

As can be seen in Table 3, 11 volatile compounds did not show any significant differences: ethyl isovalerate, E-citral, isovaleric acid, decanal, α-terpineol, D-limonene, nonanal, ethyl-9-decenoate, 2-phenylethyl acetate, octanoic acid and nonanoic acid. The factor maceration time, with a positive effect, was more influential than the factor rehydrated tomato paste in the variability of data ($P < 0.05$).

For most of cases, higher concentrations were obtained for the first day of maceration and then their values maintained with light decreases, excepting Z-citral and 6-methyl-5-hepten-2-one, which increased during maceration. Isoamyl alcohol and hexanoic acid, which have an unpleasant descriptor, reduced their concentrations after 3 days of maceration. α-terpineol, isoamyl acetate, ethyl hexanoate, ethyl octanoate, linalool, 1-octanol, ethyl decanoate, most of them associated with fruit and floral notes [30] and come mainly from alcoholic fermentation, increased initially and then they kept their concentrations.

About the factor amount of rehydrated tomato paste, it was only significant for five volatile compounds. Isoamyl acetate, isoamyl alcohol, hexanoic acid and 2-phenylethanol decreased as amount of rehydrated tomato paste increased. 6-methyl-5-hepten-2-one, which is a tomato target compound [31,32,33,34], increased in line with amount of rehydrated tomato paste. The losses observed for the former compounds could be explained taking into account the adsorption onto solids-solubilisation equilibria that took place during the process of maceration.

Principal component analysis (PCA) is a variable reduction procedure. It is useful when a high number of variables have been obtained and it is believed that there is some redundancy in those variables. Using PCA, it should be possible to reduce the observed variables into a smaller number of principal components (artificial variables) that will account for most of the variance in the observed variables.

When volatile data corresponding to maceration study were submitted to PCA, five principal components arose according to Kraiser`s criterion (eingen values >1). The first two principal components explained 51.02% of the total variance. For PC1, which explained 30.10% of the total variance, the main volatile compounds were α-terpineol, isoamyl acetate, ethyl hexanoate, ethyl octanoate, linalool, 1-octanol, 2-phenylethyl acetate, octanoic acid and decanoic acid, all of them with negative sign. Z-citral and 6-methyl-5-hepten-2-one were the main contributors to PC2.

Figure 1a shows that the distribution of all samples onto the plain defined by the first two principal components. As can be seen, both components are related to maceration time with those samples macerated during higher times with negative values for PC1 and positive values for PC2.

As can be seen, PCA results corroborated those obtained from analysis of variance.

3.2.2. Phenolic and Furanic Compounds

About the effect of maceration process on polyphenolic and furanic content, mean concentrations found for compounds considered are detailed in Table 3. Analysis of variance revealed that, in contrast to volatile compounds, the factor amount of rehydrated tomato paste was more influential than maceration time in this type of compounds. In general, the concentration in polyphenols decreased as amount of rehydrated tomato paste increased, excepting for chlorogenic acid and quercetin derivative, which are present in rehydrated tomato paste. This fact, as it was mentioned in the case of volatile compounds, could be explained taking into account possible adsorptions onto solids and/or the factor dilution that the addition of rehydrated tomato paste could provoke in the case of those compounds not present in it.

The factor time had a slightly positive effect for some of the phenolic compounds considered.

When polyphenolic and furanic compounds were submitted to principal component analysis, three PCs, which explained 73.38% of the total variance, were

extracted (eingenvalues >1). The main contributors to PC1 (48.20% of the total variance) were gallic acid, caffeic acid and quercetin-3-glucoside whereas for PC2 these ones were ρ-coumaric acid, ferulic acid and quercetin derivate, all of them with positive values.

The distribution of samples onto the plain defined by the first two principal components (Figure 1b) showed that samples with higher amount of rehydrated tomato paste exhibited positive values for PC2, however, not a clear separation of samples according to maceration time or amount of rehydrated tomato paste was obtained.

3.2.3. Sensory Analysis

Due to the optimization of a new agro-alimentary product is conditioned by the acceptability by consumers, a sensory evaluation (descriptive analysis and ranking test) was carried out. The sensory evaluation of tomato vinegars (6 g acetic acid/100 mL) macerated with different amounts of rehydrated tomato paste (3%, 5% and 7% v/v) during several days (0, 1, 3 and 7 days) revealed an increasing preference as percentage of rehydrated tomato paste increased (Friedman´s test, F_{tab}=10.88; 18 judges, 6 samples and 5% of error).

In relation to maceration time, Friedman´s test showed significant differences as maceration time increased, with higher values for those samples macerated during a higher number of days. Nevertheless, there were not significant differences between perceptions for those vinegars macerated for 3 and 7 days.

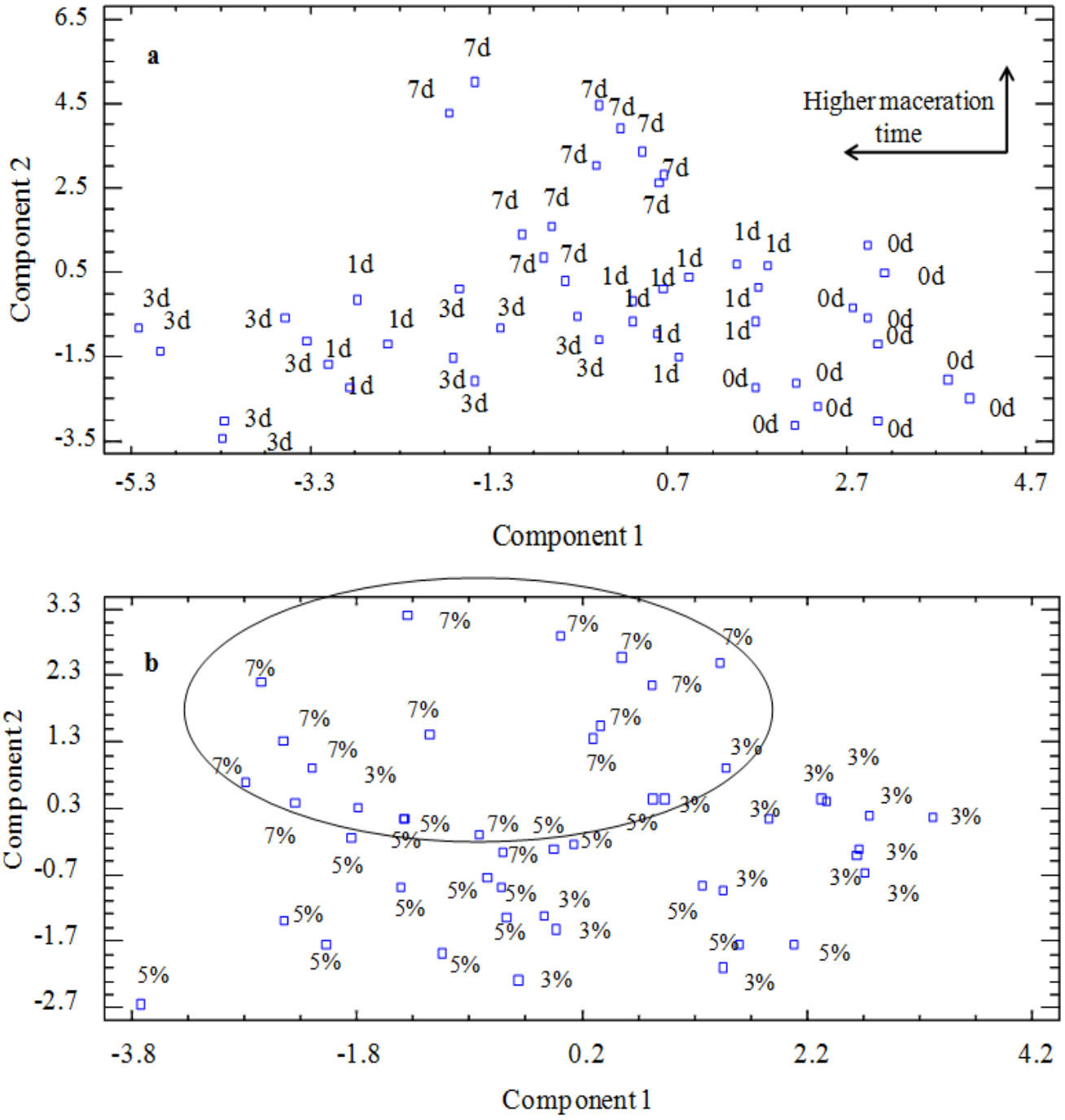

Figure 1. Principal component analysis carried out using: a: volatile data, b: phenolic and furanic data. Scatterplot of the samples onto the plane defined by the first two principal components. 0-7d: days of maceration. 3-7% amounts of rehydrated tomato paste

Table 3. Mean concentrations (μg/L, n=4) of the volatile, polyphenolic and furanic compounds in vinegars during maceration study

Volatile compounds	Maceration period (days)				Rehydrated tomato paste (% v/v)		
	0	1	3	7	3	5	7
Ethyl isovalerate	1.19	0.66	1.41	1.02	1.27	0.90	1.04
Z-Citral	0.82^{b}	0.72^{b}	0.89^{b}	1.32^{a}	0.89	1.00	0.92
E-Citral	0.91	0.46	0.98	1.12	0.92	0.75	0.95
Isovaleric acid**	3.38	4.14	4.05	3.23	4.24	3.15	3.71
Decanal*	2.95	1.63	1.60	3.44	2.04	2.73	2.44
α-Terpineol	5.60	7.68	7.63	7.77	7.73	7.27	6.33
D-Limonene	221.7	399.5	575.2	299.1	591.9	287.8	241.9
Isoamyl acetate**	0.53^{b}	0.69^{a}	0.69^{a}	0.70^{a}	0.74^{a}	0.62^{b}	0.60^{b}
Isoamyl alcohol**	64.5^{a}	66.3^{a}	63.0^{ab}	60.6^{b}	66.6^{a}	62.6^{b}	61.5^{b}
Ethyl hexanoate	0.31^{b}	2.26^{a}	2.03^{a}	2.19^{a}	1.73	1.55	1.82
6-Methyl-5-hepten-2-one	13.9^{b}	8.3^{b}	15.6^{b}	42.3^{a}	9.4^{b}	22.0^{a}	28.7^{a}
Nonanal	11.1	7.90	9.76	7.38	9.95	8.89	8.25
Ethyl octanoate	12.7^{b}	42.7^{a}	38.0^{ab}	30.3^{ab}	38.5	26.9	27.2
Linalool	3.07^{b}	5.95^{a}	4.02^{ab}	6.80^{a}	5.02	4.66	5.21
1-Octanol	5.62^{b}	9.12^{a}	8.39^{ab}	8.34^{ab}	8.41	7.50	7.69
Ethyl decanoate	8.35^{b}	20.6^{ab}	25.5^{a}	18.1^{ab}	23.3	15.7	15.4
Ethyl 9-decenoate*	7.94	7.89	8.27	7.89	8.27	7.77	7.95
2-Phenylethyl acetate**	1.60	1.77	1.68	1.73	1.76	1.70	1.63
Hexanoic acid**	2.58^{a}	2.51^{a}	2.40^{a}	2.10^{b}	2.56^{a}	2.44^{a}	2.20^{b}
2- Phenylethanol**	19.1^{a}	19.5^{a}	18.8^{ab}	17.8^{b}	19.5^{a}	19.0^{a}	17.9^{b}
Octanoic acid**	1.25	1.33	1.24	1.33	1.31	1.28	1.27
Nonanoic acid	4.46	3.75	3.47	3.53	3.76	4.06	3.58
Decanoic acid	1.09^{b}	1.55^{a}	1.36^{ab}	1.43^{a}	1.45	1.35	1.27
Phenolic and furanic Compounds							
Gallic acid**	10.12	10.12	10.00	9.95	10.34^{a}	10.07^{b}	9.74^{c}
5-hydroxy-Methylfurfural**	1.41^{c}	1.57^{b}	1.62^{b}	1.83^{a}	1.61	1.63	1.59
Caftaric acid**	2.03	2.19	2.24	2.08	2.29^{a}	2.15^{ab}	1.96^{b}
p-hydroxy-Benzoic acid**	2.71	2.52	2.75	2.69	2.65	2.82	2.52
Tyrosol**	10.28^{ab}	9.64^{b}	10.76^{ab}	11.48^{a}	11.05	10.40	10.16
Chlorogenic acid**	6.47	6.12	6.33	6.34	6.23^{b}	6.12^{b}	6.60^{a}
Caffeic acid**	3.57^{ab}	3.76^{a}	3.60^{b}	3.51^{ab}	3.77^{a}	3.61^{b}	3.46^{c}
p-Coumaric acid**	0.75	0.80	0.74	0.78	0.81^{a}	0.70^{b}	0.79^{a}
Ferulic acid**	0.58	0.57	0.57	0.56	0.60	0.55	0.57
Quercetin derivative**	57.28	56.82	55.94	53.80	53.12^{b}	52.75^{b}	62.02^{a}
Quercetin-3-glucoside**	189.03^{b}	202.90^{a}	198.69^{ab}	189.43^{b}	192.59	197.68	194.76

*Decanal: quantified by nonanal calibration curve; *Ethyl 9-decenoate: quantified by ethyl decanoate calibration curve.; **: mg/L. Significant differences for the same row are indicated with different superscript ($P < 0.05$).

4. Conclusions

Analysis of variance and principal component analysis showed significant differences in volatile compounds and polyphenols according to matrix (rehydrated tomato paste, tomato wine and tomato vinegar) and specific maceration conditions (amount of rehydrated tomato paste and time). In relation to optimum production conditions, taking sensory and compositional results into account 3 days of maceration was fixed as the best maceration time. Regarding percentage of rehydrated tomato paste, sensory analyses revealed that higher amounts were preferred, but lower polyphenolic contents were obtained as this factor increased, therefore, 5 % v/v of rehydrated tomato paste was fixed as optimum amount.

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List of Abbreviations

SBSE-GC-MS: Stir bar sorptive extraction-gas chromatography-mass
UPLC: Ultra pressure liquid chromatography
DAD: Diode array detector
UV-VIS: Ultraviolet-visible
ANOVA: Analysis of variance
PCA: Principal Component Analysis

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