Characterisation of volatiles in dried white varieties figs (*Ficus carica* L.)

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Abstract The aromatic profile of volatiles in dried figs varieties *Bružetka Bijela* and *Zimnica* were characterised by headspace solid-phase (HS-SPME) procedure with gas chromatography–mass spectrometry analysis (GC-MS). The volatile compounds were distributed by distinct chemical classes, including alcohols, aldehydes, esters, terpenic compounds, and other compounds. The figs were dried in a pilot plant cabinet dryer. Prior to drying process, figs were pre-treated by sulphur dioxide, immersed in solution of citric

acid and ascorbic acid, respectively. Several mathematical thin-layer drying models, available in the literature, were fitted to experimental data of figs, implementing non-linear regression analysis techniques. The results showed that pre-treatments of figs decrease significantly the drying time. The best thin-layer drying model in terms of fitting performance was Wang and Singh model. The major volatile compound in dried figs was benzaldehyde. After benzaldehyde, the most abundant aldehyde in dried figs was hexanal. The comparison among dried figs showed the highest abundance of aldehydes, in general, in non-treated (control) dried figs compared to pre-treated samples. Furthermore, ascorbic acid was the most efficient in preserving esters and alcohols in case of *Bružetka Bijela*, whereas in case of *Zimnica*, sulphur dioxide was in advance compared to ascorbic acid. Ethyl acetate was the most abundant ester found in dried figs. Among other compounds, 2-butanone,3-hydroxy was the most abundant identified volatiles. Linalool, as the only identified terpen, was in case of both dried fig varieties, preserved by immersion into ascorbic acid. The immersion into citric acid has not been so successful in volatiles conservation.

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Introduction

Figs (*Ficus carica* L.) are an important fresh fruit variety in many countries, as well as delicious dried fruit consumed in most parts of the world. Figs are an excellent source of minerals, vitamins, essential amino acids, sugars and organic acids. On the other hand, nutritionally, they are very low with sodium and completely fat-free. The fresh and dried

figs contain also relatively high amount of phenolic substances and other compounds with anticancer activity, like benzaldehyde and the coumarins (Vinson 1999; Slavin 2006; Solomon et al. 2006). Figs, as both a fruit and a prestigious snack food, are an ideal addition to a human diet because they represent an excellent source of fiber and are naturally sweet.

Figs are widely consumed fresh, but they are known to have a short post-harvest life. In order to prolong their storability, they are dried. Drying decreases considerably the water activity of the material, reduces microbiological activity and minimizes physical and chemical changes during its storage period (Lewicki 2006). Traditionally in tropical and subtropical countries, figs are sun-dried. Artificial drying, on the other hand, includes air-mechanical drying system. The energy sources traditionally employed are abundant, non-pollutant, renewable, cheap and environmental friendly (Basunia and Abe 2001). But there is concern about the safety of the end product, mainly because there is a risk of the development of aflatoxins. The traditional drying process is also quite labour and time consuming and causes product losses, because figs are directly exposed to climatic conditions. These concerns can be overcome by convective air drying (Piga et al. 2004). Artificial drying minimizes product losses and improves product quality because the drying parameters can be controlled and changed over the entire processing time. Excellent improvement is achieved in terms of shorter drying times and increased microbial stability (Papoff et al. 1998). The employed drying temperature can cause more or less volatile losses in the end product. The effect of drying temperature on changes in aromatic profile was considered in some research papers considering temperature as important parameter in drying process. The impact of drying temperature on changes in volatile compounds of dried longan fruit have been published by Lapsongphol et al. (2007). Longan fruits were dried at 60, 70, 80 and 90 °C using a tray dryer. The retention of cis-ocimene and beta-ocimene was found to be the highest in longan flesh dried at 70 °C. The higher drying temperature, the more 3-methyl butanal and ethyl acetate were detected. Wongpornchai et al. (2004) were investigated the effect of six drying methods namely, modified air at 30 and 40 °C, hot air at 40, 50, and 70 °C, and sun-drying on the aroma profile of rice. The methods that employed lower temperature appeared to provide higher concentrations of the key aroma compound, 2-acetyl-1-pyrroline, and lower amounts of the off-flavour compounds, n-hexanal and 2-pentylfuran. The sun-drying method showed opposite results. The retention of representative components of the apple flavour, ethyl acetate, ethyl butyrate and methyl anthranilate, during freeze and conventional drying at three different temperatures was investigated by Krokida and Philippopoulos (2006). Retention of aroma was affected

by the drying temperature and the drying method used. Lower drying temperatures and freeze drying method were suggested for maximum retention of flavour in the dried product. Recently, there have been much research on the mathematical modelling and experimental studies of the drying behaviour of figs (Babalís and Belessiotis 2004; Piga et al. 2004; Togrul and Pehlivan 2004; Doymaz 2005; Babalis et al. 2006; Xanthopoulos et al. 2007, 2009, 2010), but research on drying of pre-treated figs is still limited.

When determining fruit quality, the aromatic profile and individual volatile compounds are one of the important characteristics, which should be monitored and evaluated. Each product has a characteristic and unique composition of volatile components. The aroma of most food products consists of complicated mixtures, sometimes consisting of several hundred compounds (Plutowska and Wardencki 2007). Recently, much attention has been paid to the aroma development in dried fruit and methods leading to the improvement of aromatic characteristics in superior dried fruit production (Komes et al. 2007). Over recent years, the development of instrumental analysis in identification and concentration of volatile aromatic compounds has gained attention. The introduction of solid phase micro-extraction (SPME), as a unique sample preparation technique, offered a relative easy sampling of volatiles present in fruits. They are usually the most responsible compounds, which define the fruit aroma (Cuevas-Glory et al. 2007; Nunes et al. 2008). Moreover, SPME has the advantage of being flexible, simple, fast, sensitive and solvent free techniques (Dong et al. 2006).

We focus our research on aromatic constituents, which define the figs' odour and aroma. To our knowledge there have been published only few papers dealing with volatile compounds in figs (Gibernau et al. 1997; Grison et al. 1999; Grison-Pigé et al. 2002; Oliveira et al. 2010a, b), but there are no reports on volatile composition of white figs varieties *Bružetka Bijela* and *Zimnica*, that are commonly grown in Croatian Istria region. Figs were exposed to different drying pre-treatments and the aromatic profile was monitored. It is the first report dealing with the impact of preservatives on the final aromatic profile of dried white varieties figs.

Materials and methods

Standards and reagents

Analytical standards of volatile components were purchased from several suppliers: acetophenone, linalool, β -ionone, benzyl acetate, phenyl acetate, ethyl acetate were purchased from Fluka; α -terpineol, δ -decalactone from SAFC, FCC KOSHER; hexanal and octanal from Alfa Aesar. All

standards were >97 % pure. Ascorbic acid and citric acid were purchased from Sigma-Aldrich Chemie GmbH (Germany) and sulphur from S.T.I. Solfotecnica Italiana S.p.A. Ravenna (Italy).

Plant material

Fresh white figs cv. *Bružetka Bijela* and *Zimnica*, were collected from a fig plantation in Medulin (Croatia, GPS L:N44°48'17" 1:E13°57'2"), at the beginning of September 2010. Figs were carefully hand-picked to achieve uniform physiological state and geometric dimensions and transported immediately to the laboratory. Moisture content of fig samples was determined by oven drying to a constant weight at 105 °C (AOAC 2000). Analyses were done in triplicate. Initial moisture content for figs cv. *Bružetka Bijela* and *Zimnica* was 75.1±0.17 % and 75.8±0.09 % (wet basis), respectively.

Drying procedure

Drying of whole fig samples was performed in a pilot plant cabinet dryer (Rasadnik "Skink" Rovinj, Croatia), drying capacity 150 kg of fresh material, heater power 2×4 kW, consisting of 17 trays, each weighing 2.5 kg. The dryer was equipped with temperature and airflow velocity controllers. Drying temperature was 60 °C. Prior drying, fig samples were treated as follows: sulphuring; immersion in 0.3 % citric acid solution and immersion in 0.3 % ascorbic acid solution. Sulphuring (5 g/m³) was conducted in a separate chamber for 30 min to prevent sample browning. The drying process started when the drying conditions had been achieved. Fig samples were placed onto trays in the cabinet dryer and measurements started from this point. Sample weight loss was recorded every 10 min during drying using a digital balance. Drying lasted until a moisture content of about 25 % (wet base) was achieved.

Mathematical modelling of drying curves

The five different thin-layer drying models based on diffusion theory (Table 1), assuming that resistance to water diffusion occurs in the outer layer of the food (Brooker et al. 1992), was used to describe the changes in the moisture content and drying rates. The time-dependent weight of samples was converted for the given time dependent on the moisture content. To avoid some ambiguity in the results because of the differences in the initial sample moisture, the sample moisture was expressed as dimensionless moisture ratio ($MR = M(t)/M_0$). The drying curve for each experiment was obtained by plotting the dimensionless moisture of the sample vs. the drying time.

Table 1 Thin-layer drying models applied to the moisture ratio values of the figs

No.	Model name	Model equation	References
1	Lewis	$MR = \exp(-kt)$	Lewis 1921
2	Page	$MR = \exp(-kt^n)$	Page 1949
3	Henderson and Pabis	$MR = a \exp(-kt)$	Henderson and Pabis 1961
4	Logarithmic	$MR = a \exp(-kt) + c$	Togrul and Pehlivan 2002
5	Wang and Singh	$MR = 1 + at + bt^2$	Wang and Singh 1978

The parameters of all models were calculated by a non-linear regression method using software *Mathcad 14.0* (PTC, Needham, MA, USA). The best fitting equation was selected based on the root mean square error (RMSE) and average absolute relative deviation (AARD) as follows:

$$RMSE = \sqrt{\frac{1}{n} \sum_{i=1}^n (MR_{\text{exp}} - MR_{\text{cal}})^2} \quad (1)$$

$$AARD = \frac{1}{n} \cdot \sum_{i=1}^n \left| \frac{MR_{\text{exp}} - MR_{\text{cal}}}{MR_{\text{exp}}} \right| \cdot 100 \quad (2)$$

where MR_{exp} and MR_{cal} were the experimental and calculated dimensionless moisture ratio, respectively.

Headspace solid-phase (HS-SPME) procedure with gas chromatography–mass spectrometry analysis (GC-MS)

Extraction of aromatic compounds from dried fig samples followed the procedure of Prosen et al. (2007), with some modifications. The extraction was carried out using solid phase micro extraction fibre (SPME fibre) made of divinyl benzene-polydimethylsiloxane-carboxen stationary phase (50/30 µm DVB/Carboxen/PDMS) purchased from Supelco, Bellefonte, USA. The fibre was conditioned prior analysis according to the procedure recommendation (30 min at 270 °C). Head space vials were filled with 10 mL of deionised water to which 5 µL of internal standard (δ -deltadecalactone –0.88 mg/mL) was added. Vials were then filled with 20 (±2 %) g of previously chopped and mixed dried figs and hermetically closed with a septum stoppers. Vials containing sample were heated for 10 min at 40 °C.

A SPME fibre was inserted in the headspace and odorant compounds were sampled for 20 min. The fibre was subsequently inserted into the injector port of a gas chromatograph at 270 °C, desorbed for 10 min. Gas chromatography coupled with mass selective detector

Table 2 Curve fitting criteria for the various models and parameters for drying of fig variety Bružetka Bijela

Model no.	Fig pre-treatment	Model constants	RMSE	AARD (%)
1	Non-treated	$k=0.00050$	0.0956	15.389
	Sulphuring	$k=0.00084$	0.0324	3.8395
	Citric acid	$k=0.00099$	0.0239	3.3595
	Ascorbic acid	$k=0.00113$	0.0186	1.4895
2	Non-treated	$k=0.00013, n=1.1909$	0.0748	11.829
	Sulphuring	$k=0.00019, n=1.2325$	0.0141	1.6557
	Citric acid	$k=0.00032, n=1.1775$	0.0135	1.9259
	Ascorbic acid	$k=0.00093, n=1.0317$	0.0181	1.7157
3	Non-treated	$k=0.00063, a=1.1498$	0.0711	10.949
	Sulphuring	$k=0.00102, a=1.06364$	0.0349	5.2524
	Citric acid	$k=0.00106, a=1.03324$	0.0192	2.6849
	Ascorbic acid	$k=0.00118, a=1.02373$	0.0159	1.7075
4	Non-treated	$k=0.0003, a=1.7889, c=-0.6617$	0.0543	7.5113
	Sulphuring	$k=0.0006, a=1.4738, c=-0.4260$	0.0214	2.7959
	Citric acid	$k=0.0007, a=1.3747, c=-0.3569$	0.0156	2.2491
	Ascorbic acid	$k=0.0005, a=1.6806, c=-0.6942$	0.0279	3.9621
5	Non-treated	$a=-0.00019, b=-0.00000013$	0.0352	5.8354
	Sulphuring	$a=-0.00063, b=-0.00000007$	0.0142	1.9164
	Citric acid	$a=-0.00085, b=0.00000017$	0.0156	2.2357
	Ascorbic acid	$a=-0.00107, b=0.00000041$	0.0179	1.5339

(GC-MS–Agilent 6890 Series GC System with Agilent 5973 Mass Selective Detector– quadrupole) with a Rtx-20 column (60 m, 0.25 mmID, 1 μ m df, Restek, USA) were used for analysis of volatile compounds in

samples. The temperature program was set as follows: initial temperature of GC oven was: 50 °C/2 min, ramped for 10 °C/min–to 250 °C. Total run took 30 min. Temperature of the injector was 270 °C and

Table 3 Curve fitting criteria for the various models and parameters for drying of fig variety Zimnica

Model no.	Fig pre-treatment	Model constants	RMSE	AARD (%)
1	Non-treated	$k=0.00070$	0.1054	16.571
	Sulphuring	$k=0.00136$	0.0386	5.6801
	Citric acid	$k=0.00108$	0.0869	16.435
	Ascorbic acid	$k=0.00072$	0.0886	12.869
2	Non-treated	$k=0.00015, n=1.2176$	0.0708	16.573
	Sulphuring	$k=0.00025, n=1.2705$	0.0195	3.2655
	Citric acid	$k=0.00017, n=1.2909$	0.0570	10.973
	Ascorbic acid	$k=0.00015, n=1.2504$	0.0693	10.121
3	Non-treated	$k=0.00085, a=1.1589$	0.0743	17.063
	Sulphuring	$k=0.00149, a=1.06276$	0.0286	4.1468
	Citric acid	$k=0.00129, a=1.11859$	0.0711	13.446
	Ascorbic acid	$k=0.00090, a=1.10637$	0.0746	10.904
4	Non-treated	$k=0.00039, a=1.8782, c=-0.7634$	0.0475	8.4057
	Sulphuring	$k=0.00092, a=1.4348, c=-0.3966$	0.0245	4.0209
	Citric acid	$k=0.00053, a=2.0937, c=-1.0039$	0.0488	8.7124
	Ascorbic acid	$k=0.00089, a=1.1013, c=-0.0012$	0.0746	10.941
5	Non-treated	$a=-0.00038, b=-0.00000006$	0.0439	9.9294
	Sulphuring	$a=-0.00111, b=0.00000028$	0.0272	4.3979
	Citric acid	$a=-0.00049, b=-0.00000042$	0.0230	4.1059
	Ascorbic acid	$a=-0.00014, b=-0.00000063$	0.0232	2.9242

Fig. 1 Experimental (symbols) and predicted (lines) MR values using Wang and Singh model **a)** *Bružetka Bijela* **b)** *Zimnica*. (NT–non-treated fig, SUL–sulphuring, CA–citric acid solution, AA–ascorbic acid solution)

temperature of the detector was 280 °C. In the mass spectrometer, electron impact (EI) ionization was used and chromatograms were recorded in the total ion current (TIC) mode. Compounds were identified on the basis of their retention times (compared with standards) and spectra using the searchable EI-MS spectra library (NIST02). Peak area for quantification was measured either in TIC chromatogram or in an extracted ion chromatogram in the case of co-elution with other compounds.

Chromatographic peaks of volatiles were compared to the internal standard (IS- δ -decalactone), and expressed as a mean area with relative standard deviation, RSD (%). Samples were measured in triplicate.

Data treatment

The difference among individual treatment (pre-treatment and control) was determined by analysis of variance (ANOVA). Tukey's multiple comparison tests were performed to determine the differences between group means. All computations were carried out with SPSS Statistics 18.0 and Statistica for Windows software (StatSoft, Inc., USA).

Results and discussion

Mathematical modelling of drying curves

Convection drying of vegetable and fruits occurs in the falling rate drying period and thus semi-empirical and empirical models could be applied to the drying data. The five widely used models are shown in Table 1. The drying curves obtained were fitted with different thin-layer drying models. The root mean square error (RMSE) and average absolute relative deviation (AARD) were used as criteria for adequacy of the fit. The lowest are the RMSE and AARD values; the better is the goodness of the fit.

The calculated parameters of all applied models with their statistical analysis values for fig cv. *Bružetka Bijela* are given in Table 2 and for fig cv. *Zimnica* are given in Table 3. As can be seen from Tables 2 and 3 generally low values of RMSE and AARD were found for all drying models, but the best results were obtained with the Wang and Singh model (28). Furthermore, this model was used to describe the thin-layer drying behaviour of non-treated and pre-treated figs for both white figs varieties (Fig. 1). From Table 2 it can be seen that RMSE for Wang and Singh model ranged between 0.0142 and 0.0352, and AARD between 1.534 % and 5.835 % for all drying conditions of non-treated and pre-treated figs. In the case of fig variety *Zimnica* RMSE for Wang and Singh model ranged between 0.0230 and 0.0439, and AARD changed between 2.924 % and 9.929 % (Table 3).

RMSE and AARD values obtained with the other models (Tables 2 and 3) were higher than those in the Wang and Singh model. The Lewis model (1921) had the worst agreement between experimental and calculated values for both white fig varieties followed by the Henderson and Pabis model (1961) and Page model (1949), respectively. In general, the lowest agreements between experimental and calculated values were obtained for non-treated dried figs for all applied models. Logarithmic model (Togrul and Pehlivan 2002) show also a very good agreement between the experimental and calculated data for fig drying curves which is in accordance with the results published by Xanthopoulos et al. (2010). From the obtained results it is evident that the

Table 4 Volatile compounds identified in dried fig variety *Bružetka bijela* regarding the use of different pre-treatment (mean, relative standard deviation (RSD)) expressed as concentration of internal standard δ -decalactone (ppm = mg/kg). Means followed by the same letter

in the same row are not significantly different at $P>0.05$ according to Tukey's test. (n.s.–not significant at $P>0.05$; * $0.01 < P<0.05$; ** $0.001 < P<0.01$; *** $P<0.001$; n.d.–not detected)

Compound		Ascorbic acid		citric acid		sulphuring		control	
		Average	RSD	Average	RSD	Average	RSD	Average	RSD
Alcohols									
1 ethanol	***	2.67 c	0.16	2.28 bc	0.02	1.79 ab	0.17	1.14 a	0.1
2 1-butanol, 3-methyl-	***	3.73 d	0.01	2.53 c	0.1	1.42 b	0.05	0.71 a	0.09
3 1-butanol, 2-methyl-	***	0.99 c	0.07	1.02 c	0.08	0.61 b	0.08	n.d. a	/
4 1-hexanol	***	0.79 c	0.17	0.24 b	0	n.d. a	/	0.65 c	0.02
5 1-octen-3-ol	**	0.29 a	0.23	0.30 a	0.03	0.12 a	0	0.54 b	0.04
Aldehydes									
6 butanal, 3-methyl-	***	4.79 b	0	5.26 bc	0.05	3.36 a	0.05	5.79 c	0
7 butanal, 2-methyl-	**	2.03 a	0.07	2.70 a	0.02	2.30 a	0.15	4.06 b	0.1
8 pentanal	**	2.72 a	0.04	3.62 b	0.08	2.43 a	0.03	3.87 b	0.05
9 hexanal	***	15.8 b	0.02	12.9 b	0.08	8.27 a	0.09	23.8 c	0.03
10 2-hexenal, (E)-	n.s.	1.30	0.05	0.97	0.11	1.46	0.63	0.31	0.11
11 furfural	**	5.56 a	0.11	4.85 a	0.14	4.88 a	0.03	9.69 b	0.03
12 heptanal	*	1.14 ab	0.05	0.82 a	0.01	0.80 a	0.19	1.55 b	0.19
13 2,4-hexadienal, (E,E)-	***	0.24 ab	0.11	n.d. a	/	0.36 bc	0.32	0.55 c	0.19
14 2-nonenal, (E)-	n.s.	0.22	0.08	0.28	0.31	0.22	0.2	0.26	0.05
15 2-heptenal, (Z)-	*	0.66 a	0.25	0.71 ab	0.06	0.65 a	0.29	1.09 b	0.05
16 benzaldehyde	***	43.4 b	0.1	32.1 ab	0.05	63.9 c	0.14	24.7 a	0.06
17 2,4-heptadienal, (E,E)-	***	0.45 c	0.17	0.46 c	0.1	n.d. a	/	0.23 b	0.09
18 2-octenal, (E)-	**	0.39 a	0.22	0.35 a	0.02	0.15 a	0	0.76 b	0
19 nonanal	**	0.30 a	0.26	0.29 a	0.02	0.38 a	0.04	0.71 b	0.04
20 benzeneacetaldehyde	***	0.38 b	0.22	0.33 b	0.11	0.12 a	0.15	0.62 c	0.01
21 benzaldehyde, 3-ethyl-	***	0.10 c	0.01	0.09 b	0.03	n.d. a	/	n.d. a	/
Esters									
22 acetic acid, methyl ester	n.s.	0.39	0.27	1.32	0.04	1.78	0.4	0.14	0
23 ethyl acetate	*	19.5 b	0.06	25.7 b	0.05	55.2 c	0.19	2.98 a	0.01
24 butanoic acid, ethyl ester	n.s.	0.49	0.07	0.30	0.04	0.45	0.7	0.22	0.09
25 butanoic acid, 2-methyl-, ethyl ester	***	0.27 b	0.06	0.27 b	0.04	0.18 a	0.04	0.18 a	0.03
26 butanoic acid, 3-methyl-, ethyl ester	***	0.18 c	0.09	n.d. a	/	n.d. a	/	0.14 b	0.1
27 2-butenic acid, ethyl ester, (E)-	n.s.	0.55	0.07	0.16	0.19	0.22	0	0.58	0.29
28 1-butanol, 3-methyl-, acetate	***	0.73 a	0.04	0.67 a	0.05	3.57 b	0.51	0.41 a	0.1
29 hexanoic acid, ethyl ester	***	5.42 d	0.06	2.60 b	0.03	4.06 c	0	n.d. a	/
30 hexanoic acid, 5-methyl-, methyl ester	**	0.23 b	0.4	0.21 b	0.1	n.d. a	/	n.d. a	/
31 heptanoic acid, ethyl ester	**	0.36 b	0.3	0.21 b	0.03	0.27 b	0	n.d. a	/
32 octanoic acid, ethyl ester	**	0.41 c	0.27	0.29 bc	0.1	0.12 ab	0.02	n.d. a	/
33 methyl salicylate	***	0.24 b	0.12	0.15 b	0	0.76 c	0.11	n.d. a	/
Acids									
34 acetic acid	*	1.15 ab	0.2	1.69 b	0.15	0.82 a	0.24	0.74 a	0.14
35 hexanoic acid	***	n.d. a	/	n.d. a	/	n.d. a	/	0.39 b	0.03
Terpens, and terpenic compounds									
36 linalool oxide	***	n.d. a	/	n.d. a	/	0.14 a	0.06	0.21 c	0.11
37 linalool	**	0.92 c	0.24	0.81 bc	0.08	0.45 ab	0.09	0.41 a	0.06
Other compounds									
38 2,3-butanedione	*	2.18 b	0.02	1.76 ab	0.28	0.82 a	0.01	0.83 a	0.16
39 furan, tetrahydro-	***	0.32 a	0.09	0.53 a	0.44	7.58 b	0.08	0.64 a	0.11

Table 4 (continued)

Compound		Ascorbic acid		citric acid		sulphuring		control	
		Average	RSD	Average	RSD	Average	RSD	Average	RSD
40 furan, 2-ethyl-	***	0.59 c	0.13	0.29 b	0.05	n.d. a	/	0.94 d	0.05
41 2-butanone, 3-hydroxy-	***	6.14 c	0.08	4.81 bc	0.18	2.35 ab	0	0 a	0
42 oxime-, methoxy-phenyl-	n.s.	0.74	0.07	0.66	0	0.75	0.16	0.94	0.05
43 furan, 2-pentyl-	***	n.d. a	/	n.d. a	/	1.88 b	0.32	2.95 b	0.15
44 5-hepten-2-one, 6-methyl-	**	0.79 b	0.17	0.35 a	0.06	0.35 a	0.29	0.56 ab	0.11
45 butyrolactone	*	1.59 ab	0.11	1.42 a	0.12	1.39 a	0.05	2.25 b	0.12
46 acetophenone	**	0.30 bc	0.16	0.35 c	0.16	0.14 ab	0	n.d. a	/
Internal standard									
δ-decalactone	***	0.12 a	0.15	0.09 a	0.02	0.15 a	0.26	0.25 b	0.11

more coefficients introduced in the model, the more accurate predictions are obtained.

From Fig. 1 it can be observed very good agreement between the experimental data (moisture ratio vs. drying time) for pre-treated figs cv. *Bružetka Bijela* and *Zimnica* and the approximation data using the Wang and Singh model, while in the case of non-treated figs agreement between experimental and calculated data was worst. As indicated in these curves, there was no constant drying rate period in the drying of figs. Drying process occurred during the falling rate drying period. During the falling drying rate period, the predominant mechanism of mass transfer was diffusion. Furthermore, from the data in Fig. 1 it is obvious that drying pre-treatments of figs resulted in a reduction, by about 50 % of the drying time compared with non-treated figs (from 27 h up to 13 h depending on used pre-treatment). In fruit such as figs that are rich in sugar, pre-treatments cause micro wounds on the peel and removes waxy layers, thus enhancing water transfer from the figs. In general, pre-treatments before drying reduced non-enzymatic browning and speed the drying process (Togrul and Pehlivan 2002; Piga et al. 2004).

Volatiles present in dried figs

The effect of the drying process on the characteristic aroma structure of figs white varieties *Bružetka Bijela* and *Zimnica* is shown in Tables 4 and 5. When comparing varieties, only 4 alcohols were present in both dried figs varieties, *Bružetka Bijela* and *Zimnica*, whereas 1-butanol, 2-methyl (3) was present only in *Bružetka Bijela* and 1-butanol (47), 5-hepten-2-ol, 6-methyl (48), 1-heptanol (49), and 1-octanol (50) only in *Zimnica*. The most interesting observation comes from the fact, that 2-methyl-butanol (3) (organoleptic description: as roasted wine, onion, fruity) was absent in control of dried fig variety *Bružetka bijela*, but it was present in

higher amount, when acidic pre-treatment was employed during the drying process. Its isomer 3-methyl-butanol (2) was found as one of the major constituents of volatile alcohols in southern, or/and exotic fruit (Jordán et al. 2001, 2002; Pino et al. 2003). In case of *Bružetka Bijela* dried fig samples, 4 volatiles, from the group of alcohols, were predominantly conserved by ascorbic acid; ethanol (1), 3-methyl-butanol (2), 2-methyl-butanol (3) and 1-hexanol (4), whereas 1-octen-3-ol (5) was higher in control samples. In case of *Zimnica*, on the other hand, the highest amount of alcohols was found in control dried figs whereas only ethanol (1) was higher in all pre-treated samples compared to dried figs in the control. It is probable that this arose from ethanol producing yeasts found in figs (Rao et al. 2008), as time consuming pre-treatment resulted in higher yeast activity in figs.

The group of aldehydes was the most sensitive group of volatiles. The results collected in Tables 4 and 5, where volatiles are sorted according to pre-treatment and group, indicate the susceptibility of aldehydes to drying procedure. The identified aldehydes average concentration is lower in the pretreated samples than in the control. In fact, in production of raisins, aldehydes, such as (E)-2-heptenal, (E)-2-nonenal (14), (E)-2-octenal (18), (E,E)-2,4-decadienal and (E,E)-2,4-nonadienal were reported to derive from unsaturated fatty acid oxidative degradation and that they have a high probability of contributing to the total aroma/flavour of raisins, because of their significant odour threshold (Buttery 2010).

Ethyl acetate (23) was the most abundant ester in pre-treated dried figs, with the higher content found in samples, which were treated with sulphur. It was followed by hexanoic acid, ethyl ester (29) found in *Bružetka Bijela* and methyl salicylate (33) in *Zimnica*. The ethyl acetate formation is closely related to ethanol formation and its increase was expected in all pre-

Table 5 Volatile compounds identified in dried fig variety *Zimnica* regarding the use of different pre-treatment (mean, relative standard deviation (RSD)) expressed as concentration of internal standard δ -decalactone (ppm = mg/kg). Means followed by the same letter in

the same row are not significantly different at $P>0.05$ according to Tukey's test. (n.s.–not significant at $P>0.05$; * $0.01 < P<0.05$; ** $0.001 < P<0.01$; *** $P<0.001$; n.d.–not detected)

Compound		Ascorbic acid		citric acid		sulphuring		control	
			RSD		RSD		RSD		RSD
Alcohols									
1 ethanol	*	3.04 b	0.2	2.70 b	0.18	2.62 b	0.08	1.05 a	0.05
47 1-butanol	***	n.d. a	/	n.d. a	/	1.97 b	0.04	n.d. a	/
2 1-butanol, 3-methyl-	***	1.07 b	0.08	1.19 b	0.11	2.00 c	0.01	0.35 a	0.15
48 5-hepten-2-ol, 6-methyl-	***	n.d. a	/	n.d. a	/	n.d. a	/	8.75 b	0.37
4 1-hexanol	***	n.d. a	/	n.d. a	/	n.d. a	/	0.87 b	0.01
49 1-heptanol	***	n.d. a	/	n.d. a	/	n.d. a	/	0.67 b	0.1
5 1-octen-3-ol	***	0.28 a	0.02	0.25 a	0.02	0.27 a	0.15	2.28 b	0.30
50 1-octanol	***	n.d. a	/	0.06 a	0	n.d. a	/	0.72 b	0.19
Aldehydes									
6 butanal, 3-methyl-	*	4.29 ab	0.09	3.97 a	0.06	4.57ab	0.06	6.48 b	0.20
7 butanal, 2-methyl-	n.s.	2.57	0.44	2.84	0.16	3.26	0.03	4.65	0.00
8 pentanal	***	1.79 a	0.05	1.82 a	0.05	1.75 a	0.19	6.25 b	0.01
9 hexanal	***	7.20 a	0.02	9.74 a	0.07	11.7 a	0.06	55.7 b	0.21
10 2-hexenal, (E)-	***	0.91 b	0.05	0.95 b	0.06	1.27 c	0.03	0.61 a	0.02
11 furfural	***	n.d a	/	n.d. a	/	n.d. a	/	11.9 b	0.13
12 heptanal	***	0.22 a	0.09	0.39 a	0.19	0.35 a	0.14	3.88 b	0.06
15 2-heptenal, (Z)-	***	0.44 a	0.04	0.47 a	0.05	0.43 a	0.1	2.48 b	0.1
51 octanal	***	n.d. a	/	0.39 a	0.01	0.43 a	0.01	2.21 b	0.26
52 2-furancarboxaldehyde, 5-methyl-	***	n.d. a	/	n.d. a	/	n.d. a	/	0.61 b	0.05
16 benzaldehyde	**	82.7 b	0.01	56.0 a	0.05	57.9 a	0.06	64.6 a	0.13
17 2,4-heptadienal, (E,E)-	*	0.39 ab	0.15	0.33 a	0.2	0.33 a	0.07	0.55 b	0.11
18 2-octenal, (E)-	***	0.28 a	0.05	0.32 a	0.07	0.37 a	0.04	2.60 b	0.11
19 nonanal	***	0.31 a	0.01	0.26 a	0.05	0.21 a	0.07	0.74 b	0.17
20 benzeneacetaldehyde	***	0.37 a	0.03	0.32 a	0.05	0.35 a	0.03	0.94 b	0.11
21 benzaldehyde, 3-ethyl-	***	n.d. a	/	0.06 a	0	n.d. a	/	0.29 b	0.12
53 p-menth-1-en-9-al	***	n.d. a	/	0.11 b	0	n.d. a	/	0.17 b	0.26
Esters									
22 acetic acid, methyl ester	**	0.53 ab	0.49	0.96 b	0.32	0.68 b	0.36	n.d. a	/
23 ethyl acetate	***	9.68 b	0.25	11.5 b	0.07	16.8 c	0.05	1.31 a	0.05
25 butanoic acid, 2-methyl-, ethyl ester	***	0.10 a	0.16	0.09 a	0.04	0.26 b	0.1	0.13 a	0.15
28 1-butanol, 3-methyl-, acetate	***	0.15 c	0.09	0.11 b	0	0.21 d	0.03	n.d. a	/
29 hexanoic acid, ethyl ester	***	1.94 c	0.03	1.36 b	0.09	2.04 c	0.03	n.d. a	/
54 benzoic acid, methyl ester	***	n.d. a	/	n.d. a	/	0.20 b	0.07	n.d. a	/
32 octanoic acid, ethyl ester	***	0.39 c	0.08	0.19 a	0.1	0.32 b	0.03	0.19 a	0.01
55 benzoic acid, ethyl ester	***	n.d. a	/	n.d. a	/	0.14 b	0.12	n.d. a	/
33 methyl salicylate	***	2.73 b	0.12	6.16 c	0.06	5.13 c	0.12	1.17 a	0.39
56 benzoic acid, 2-hydroxy-, ethyl ester	***	0.14 b	0.03	n.d. a	/	0.30 c	0.07	n.d. a	/
Acids									
34 acetic acid	***	1.65 b	0.04	2.96 c	0	2.48 c	0.11	0.64 a	0.08
35 hexanoic acid	***	n.d. a	/	n.d. a	/	n.d. a	/	1.03 b	0.38
Terpens, and terpenic compounds									
36 linalool oxide	***	0.24 a	0.05	0.17 a	0.05	0.20 a	0.11	0.65 b	0.12
37 linalool	***	0.92 c	0.05	0.31 a	0.11	0.56 b	0.14	0.75 bc	0.14
57 2 H-pyran-3-ol, 6-ethenyltetrahydro-2,2,6-trimethyl-epoxylinalol	***	0.41 c	0.01	0.30 b	0.09	0.27 b	0.08	n.d. a	/

Table 5 (continued)

Compound		Ascorbic acid		citric acid		sulphuring		control	
		RSD		RSD		RSD		RSD	
Other compounds									
38 2,3-butanedione	***	3.90 b	0.02	5.53 c	0	4.10 b	0.03	0.82 a	0.02
58 furan, 2-methyl-	***	n.d. a	/	n.d. a	/	n.d. a	/	0.46 b	0.02
39 furan, tetrahydro-	***	0.20 b	0.27	n.d. a	/	n.d. a	/	0.07 a	0.04
40 furan, 2-ethyl-	***	n.d. a	/	n.d. a	/	n.d. a	/	1.77 b	0.15
41 2-butanone, 3-hydroxy-	***	11.3 b	0.01	18.5 c	0.04	12.7 b	0.01	1.69 a	0.07
42 oxime-, methoxy-phenyl-	**	0.43 a	0.08	0.51 a	0.13	0.52 a	0.05	0.78 b	0.09
43 furan, 2-pentyl-	***	n.d. a	/	n.d. a	/	n.d. a	/	16.3 b	0.17
59 2-octanone	***	n.d. a	/	n.d. a	/	n.d. a	/	1.15 b	0.17
44 5-hepten-2-one, 6-methyl-	***	0.26 a	0.08	0.20 a	0.01	0.28 a	0.13	1.39 b	0.24
45 butyrolactone	***	1.05 c	0.03	0.48 b	0.48	0.35 b	0.14	n.d. a	/
46 acetophenone	***	0.17 a	0.04	0.15 a	0.01	0.16 a	0.13	0.65 b	0.24
60 damascenone	***	n.d. a	/	0.06 a	0.60	n.d. a	/	0.16 b	0.22
Internal standard									
δ-decalactone	*	0.11 ab	0.03	0.12 ab	0.35	0.07 a	0.11	0.22 b	0.31

treated samples. Ester with a fruity odour, the so called banana oil, 1-butanol-3-methyl acetate (**28**) was found only in dried figs of both varieties. It was the best preserved by sulphurization. The hexanoic acid, ethyl ester (**29**) (odour similar to banana and pineapple) were identified in dried figs of both varieties, no matter the pre-treatment used.

Komes et al. (2007) have found that hexyl acetate being on an average twice as high in pears before dehydration. Octanoic acid, ethyl ester (**32**) (fruity like apple, pine apple, brandy nuance), found in both varieties, was preserved the best by immersion into ascorbic acid. Similar also butanoic acid, 2-methyl-ethyl ester (**25**), butanoic acid, 3-methyl-ethyl ester (**26**), hexanoic acid, ethyl ester (**29**), hexanoic acid, 5-methyl-methyl ester (**30**) and heptanoic acid, ethyl ester (**31**) were preserved in ascorbic acid in case of *Bružetka Bijela*. Contrary, in case of *Zimnica* the conservation of esters was more efficient by applying sulphurization. In literature, there are no data available to compare the obtained results, authors, however, noticed similar observation, when esters found in bananas were monitored during drying, some of them decreased, some of them increased compared to amount of esters present in fresh fruit (Boudhrioua et al. 2003).

The only identified terpenes in dried figs were linalool (**37**), linalool oxide (**36**) and epoxy linalool (**57**) in the case of *Zimnica*. Linalool was better preserved by ascorbic acid, whereas linalool oxide was in higher amount found in control samples of both fig varieties. Linalool was also the major terpenoid found in dried nectarines (Sunthonvit et al. 2007).

Conclusions

This is the first study comparing the aromatic profile of volatiles in dried figs of the Croatian white cultivars *Bružetka Bijela* and *Zimnica*. The volatile profiles of figs were characterised by HS-SPME and GC-MS. Prior to drying in a pilot plant cabinet dryer, figs were pre-treated by sulphur dioxide and immersed in solution of citric acid and ascorbic acid, respectively. The adaptability of a thin-layer drying model to whole figs was investigated. The best fitting equation was selected based on the root mean square error and average absolute relative deviation where the best results were obtained using Wang and Singh model. Pre-treatments of figs decreased drying time for about 50 % compared with non-treated figs.

The analysis of aromatic profile of white varieties figs show that the group of aldehydes was the most susceptible group of volatiles. Longer drying time resulted in higher abundance of aldehydes in non-treated dried figs. Ascorbic acid was the most efficient in preserving esters in case of *Bružetka Bijela*, whereas in case of *Zimnica*, sulphur dioxide was in advance compared to ascorbic acid. The immersion into citric acid has not been so successful in volatiles conservation.

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