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SHORT COMMUNICATION

Vinegar production from fruit concentrates: effect on volatile composition and antioxidant activity

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Abstract Vinegar stands as a highly appreciated fermented food product due to several functional properties and multiple applications. This work focuses on vinegar production from fruit wines derived from fruit concentrates, to attain a food product with nutritional added value. Four fruit vinegars (orange, mango, cherry and banana), were produced and characterized, with total acidities of $5.3 \pm 0.3\%$ for orange, $5.6 \pm 0.2\%$ for mango, $4.9 \pm 0.4\%$ for cherry and $5.4 \pm 0.4\%$ for banana. Acetification showed impact on aroma volatiles, mainly related to oxidative reactions. Minor volatiles associated with varietal aroma were identified, monoterpenic alcohols in orange vinegar, esters in banana vinegar, C_{13}-norisoprenoids in cherry vinegar and lactones in mango vinegar, indicating fruit vinegars differentiated sensory quality. Total antioxidant activity analysis by FRAP, revealed fruit vinegars potential to preserve and deliver fruit functional properties. Antioxidant activity of fruit vinegars, expressed as equivalents of Fe_2SO_4, was of 11.0 ± 1.67 mmol L^{-1} for orange, 4.8 ± 0.5 mmol L^{-1} for mango, 18.6 ± 2.33 mmol L^{-1} for cherry and 3.7 ± 0.3 mmol L^{-1} for banana. Therefore, fruit vinegars presented antioxidant activity close to the reported for the corresponding fruit, and between 8 and 40 folds higher than the one found in commercial cider vinegar, demonstrating the high functional potential of these novel vinegar products.

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Introduction

Consumer concern and increasing knowledge about nutritional impact on human health lead to the advance of preventive medicine and nutraceuticals, a novel generation of food products with functional properties (Lobo et al. 2010). Vinegar is widely acknowledged by its functional features possessing antimicrobial properties, antioxidant activity, dietary, antidiabetic and antitumoral effect, as well as preventing cardiovascular diseases (Budak et al. 2014). Also highly acknowledged, fruit represent one of the main sources of nutrients with functional properties, being a source of phytochemicals with antioxidant activity, as well as flavors, colors and aromas. Antioxidants present in fruits have already been correlated with nutritional benefits, due to their ability to scavenge and inhibit free radicals formed during oxidative metabolism with harmful effects for human health (Gülçin 2012). Therefore, there is high interest on developing strategies for the delivery of such nutrients and vinegar poses as a strong candidate for the design of an enhanced functional food. Vinegar is not only an ingredient for food seasoning but also a main ingredient for formulation of beverages. Thus the market for vinegar related products is expected to grow, along with the demand for genuine, high quality fruit vinegar products (Chang et al. 2005).

New and improved products derived from vinegar are now starting to be developed and studied that fruit inclusion has a major role (Cejudo-Bastante et al. 2013). Fruit vinegar designation is also valid for products obtained by mixing juice with vinegar (Chang et al. 2005). However,

considering consumer interest on quality and genuine food products, the establishment of vinegars produced solely from fruits is of upmost importance to guarantee a final product with fruit natural properties.

In a recent trend, some works have been reported on fruit vinegars characterization, focusing on specific features of the product including major volatile analysis of persimmon and strawberry vinegars (Ubeda et al. 2011) and antioxidant features of rabbiteye blueberry vinegar pomace (Su and Silva 2006). In an effort to a more global approach, this work presents an overall analysis of process dynamics, chemical composition and antioxidant activity of four novel orange, mango, cherry and banana vinegars, produced from whole fruit concentrates.

Materials and methods

Chemicals

The following chemicals were used for the standards: citric acid monohydrate (99.5%) (Merck), absolute ethanol (99.5%) (Panreac), L(−)-Malic Acid (99%) (Acros Organics), acetic acid glacial (99.7%). For GC-FID the following standards were used: acetaldehyde (≥99.5%), methyl acetate (≥99.9%), 1-propanol (≥99.9%), 2-methyl-1-propanol (≥99.8%), 2-methyl-1-butanol (≥98%), 3-methyl-1-butanol (≥99.8%), 2,3-butanediol, *levo* (≥99.0%), 2,3-butanediol, *meso* (≥99.0%) from (Fluka) and ethyl acetate (99.8%), methanol (≥99.8%), diethyl succinate (99.0%) from (Sigma-Aldrich). For GC–MS: 1-octanol (≥99.5%), furfuryl alcohol (≥98%), 1-dodecanol (≥98.5%), isobutyl acetate (≥98.5%), 2-phenylethyl acetate (≥99.0%), fenchol (≥99.0%), borneol (>95.0%), *trans*-furan linalool oxide and *cis*-furan linalool oxide (≥97.0%), isobutyric acid (≥99.5%), butyric acid (≥99.5%), hexanoic acid (≥98.0%), decanoic acid (≥98.0%), benzaldehyde (≥99.0%), acetoin (≥97.0%) from Fluka, 3-ethoxy-1-propanol (97%), benzyl alcohol (≥99.0%), ethyl butyrate (99.0%), 3-methylbutyl acetate (≥99.0%), ethyl hexanoate (≥99.9%), *Z*-3-hexenyl acetate (≥98%), ethyl octanoate (≥99.0%), ethyl 3-hydroxybutyrate (99.0%), ethyl decanoate (≥99.0%), benzyl acetate (≥99.0%), linalool (97%), terpinen-4-ol (≥99.0%), β-citronellol (95%), nerol (97%), geraniol (98%), eugenol (99%), 4-vinylguaiacol (≥98%), 4-vinylphenol (12%), acetovanillone (98%), zingerone (≥96%), 3-methylbutyric acid (99%), 2-methylbutyric acid (98%), octanoic acid (≥99.5%), isovaleric acid (99%) methoxyfuraneol (≥97%), furaneol (≥98%), γ-decalactone (≥98%), 2-methyltetrahydrothiophen-3-one (≥97%), 2-(methylthio)ethanol (99%), methionol (98%), 6-methyl-5-hepten-2-one (99%) from Sigma-Aldrich, isopulegol (>85.0%) from TCI, myrcenol (≥90.0%) from Ventós and α-terpineol (≥98.0%) from Merck. For the FRAP assay the following reagents were used: 2,4,6-tris(2-pyridyl)-s-triazine (≥98%), Iron(III) chloride (>97%) and sodium acetate (≥99%), all from Sigma-Aldrich.

Fruit vinegar production

For the production of fruit vinegars, fruit wines were produced from fruit concentrates in the previously optimized conditions (Coelho et al. 2015). Fruit wines were then centrifuged at 10,000*g* during 15 min to remove yeast and suspended solids. After ethanol quantification, fruit wines were diluted with sterile water to the desired initial alcoholic strength and inoculated with a natural isolate of acetic bacteria (confirmed as *Acetobacter* sp.), previously grown in YE medium [1% (m/v) yeast extract and 6% (v/v) ethanol] and collected by centrifugation at 4000 min^{-1} during 15 min, re-suspended in the diluted fruit wine in a pre-inoculum/diluted fruit wine volumetric ratio of 1:2. Then 100 mL acetic fermentations were conducted in triplicate in Erlenmeyer flasks fitted with cotton stoppers allowing gas exchange, at 30 °C with 200 min^{-1} orbital agitation. Acetification was monitored by periodical sampling and measurement of total acidity by colorimetric titration with 0.1 mol L^{-1} NaOH, using 1% phenolphthalein as indicator. Samples were also collected to follow ethanol-acetic acid conversion.

Fruit vinegars characterization

Ethanol and organic acids

Ethanol and organic acids were measured by high performance liquid chromatography using a Varian Metacarb 87H column and H_2SO_4 5 mmol L^{-1} mobile phase at 0.7 mL min^{-1}. Organic acids were measured using a Jasco 870-UV detector at 210 nm and ethanol was measured using a Jasco RI-1530 detector. Calibration curves from pure standards were used for quantification.

Antioxidant activity

Antioxidant activity was quantified using Ferric Reducing Antioxidant Power (FRAP) assay. 10 µL of each sample was mixed, in a 96 well microplate, with 290 µL of FRAP reagent. FRAP reagent used in the assay was prepared by mixing a 10 mmol L^{-1} 2,4,6-tris (1-pyridyl)-5-triazine (TPTZ) solution (made with 40 mmol L^{-1} HCl) with a 20 mmol L^{-1} $FeCl_3$ solution and 300 mmol L^{-1} acetate buffer (pH 3.6) in a 1:1:10 volumetric proportion. Samples were incubated at 37 °C during 15 min followed by absorbance measurement at 593 nm. Antioxidant activity was expressed as Fe_2SO_4 equivalents, using the proper calibration curve.

Major volatile compounds

Major volatile compounds were quantified using a Chrompack CP-9000 gas chromatograph with a split/splitless injector, a flame ionization detector (FID) and a capillary column, coated with CP-Wax 57CB (50 m × 0.25 mm; 0.2 μm film thickness, Chrompack), by direct injection of the samples with 4-nonanol as internal standard. Injector and detector temperatures were 250 °C. Oven temperature was initially held at 60 °C, for 5 min, then programmed to rise from 60 to 220 °C, at 3 °C min^{-1}, and maintained at 220 °C for 10 min. Carrier gas was helium 4× (Praxair) at a flow rate of 1 mL min^{-1} (125 kPa at the head of the column). 1 μL of sample was injected in split mode (15 mL min^{-1}) for analysis. Quantification was performed using software Star-Chromatography Workstation version 6.41 (Varian) supported by response factors and retention times determined with pure standards. Independent fermentation triplicates were analyzed for determination of experimental deviations.

Minor volatile compounds

Minor volatiles were analyzed by GC–MS after extraction of 8 mL of fruit vinegar with 400 μL of dichloromethane, with 3-octanol as internal standard. A gas chromatograph Varian 3800 with a 1079 injector and an ion-trap mass spectrometer Varian Saturn 2000 was used. 1 μL injections were made in splitless mode (30 s) in a Sapiens-Wax MS column (30 m × 0.15 mm; 0.15 μm film thickness, Teknokroma). Carrier gas was helium 4× (Praxair) at a constant 1.3 mL min^{-1} flow. Detector was set to electronic impact mode with an ionization energy of 70 eV, a mass acquisition range from 35 to 260 *m/z* and 610 ms acquisition interval. Oven temperature was initially set to 60 °C for 2 min and then raised from 60 to 234 °C at a rate of 3 °C min^{-1}, raised from 234 to 250 °C at 10 °C min^{-1} and finally maintained at 250 °C for 10 min. Injector temperature was 250 °C with 30 mL min^{-1} split flow. Compounds were identified using MS Workstation version 6.9 (Varian) software, by comparing mass spectra and retention indices with those of pure standards. Minor compounds were quantified as 3-octanol equivalents. Independent fermentation triplicates were analyzed for determination of experimental deviations.

Results and discussion

Production of fruit vinegars

Alcoholic fermentation allowed the production of fruit wines with alcoholic strengths (v/v) of 8.6 ± 0.22%, 11 ± 0.70%, 7.9 ± 0.72%, 11.5 ± 2.08% for orange, mango, cherry and banana respectively, coherent with the previously described (Coelho et al. 2015) and within concentrations feasible for vinegar production. Total acidity profiles, represented in Fig. 1), allowed acetification profiling. As seen, it was possible to produce vinegar from all fruit wines, with total acidities between 5 and 6% (m/v), as required. Initial total acidity was similar for orange and cherry, higher than the one observed for banana and mango, due to fruits natural composition. Orange, cherry and banana acetifications presented a 50 h lag phase whereas mango initiated acetification immediately. All acetifications reached stationary phase between 130 and 150 h of fermentation. Ethanol/acetic acid conversion profiles are presented in Fig. 1). In most cases, a slight decrease of acetic acid concentration at the end of acetification was observed, which can be linked to acetic acid over oxidation due to substrate depletion (Gullo and Giudici 2008). Acetic acid reached maximum concentration between 40 and 50 g L^{-1}. Such values don't fit the total acidity measured, being complemented by additional organic acids. Citric acid was found in fruit vinegars at 17.5 ± 0.26 g L^{-1} for orange, 4.9 ± 0.11 g L^{-1} for mango, 2.4 ± 0.16 g L^{-1} for cherry and 2.6 ± 0.06 g L^{-1} for banana vinegar. Malic acid was only found in cherry and banana vinegars in the concentrations of 18.4 ± 0.22 and 2.0 ± 0.05 g L^{-1} respectively. Thus, fruit vinegars possessed lower content of acetic acid when compared to traditional wine vinegars for the same total acidity, due to the presence of fruit characteristic organic acids. Final ethanol concentration was residual but ethanol-acetic acid conversion efficiency was rather low, at percentages of the theoretical yield of 45 ± 1% in orange, 52 ± 2% in mango, 55 ± 2% in cherry and 55 ± 4% in banana acetifications. This low efficiency can be expected when taking into account the system used for acetification, the method and long fermentation times, leading to ethanol losses by evaporation. Acetic acid yield and productivity can be further improved by alternative methods/setups for acetification, which is out of the scope of the current work.

Characterization of volatile composition

Major volatile compounds

Nine major volatile compounds were identified by GC-FID in the fruit vinegars, as presented in Table 1. Overall major volatile compound content in fruit vinegars was considerably lower when compared to the reported for the corresponding fruit wines. Apart from the dilution for acetification, major volatile compound losses can also be related to evaporation due to the long acetification time and/or to non-specific oxidations performed by acetic bacteria. Fruit vinegars showed lower acetaldehyde content

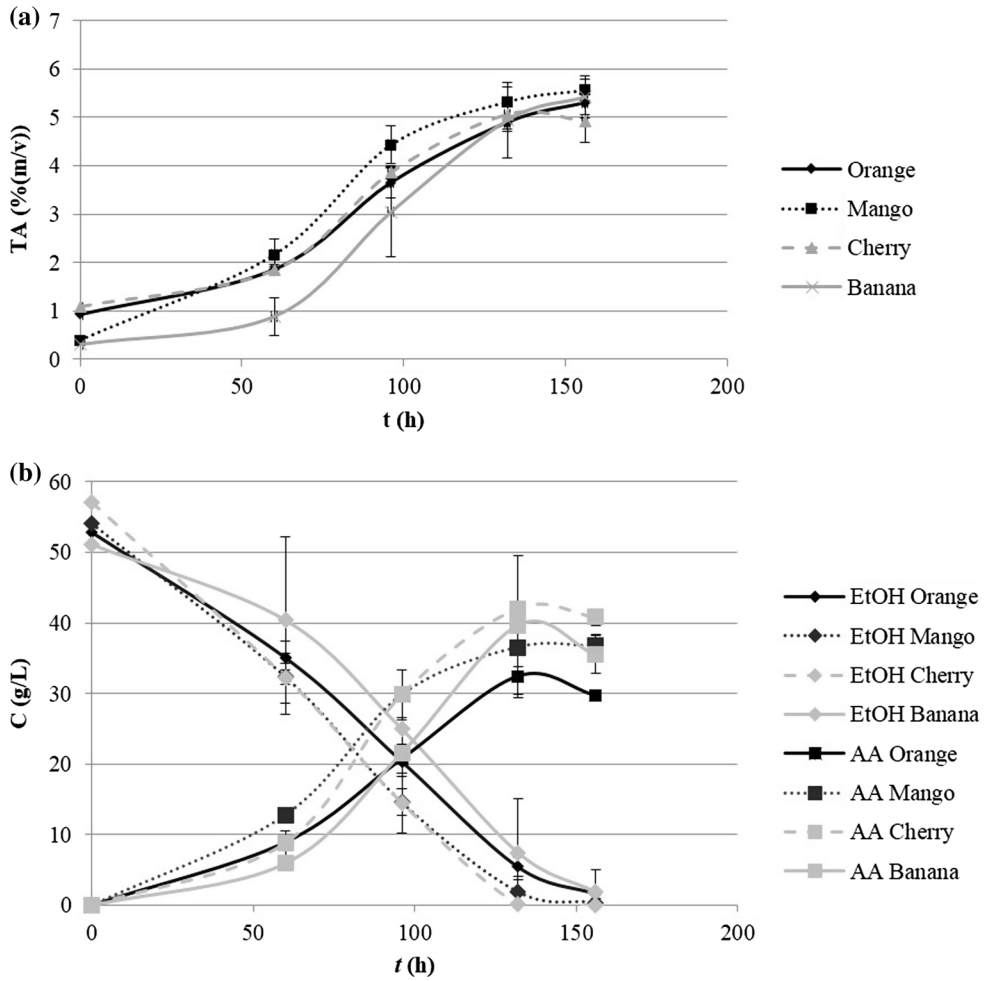

Fig. 1 Acetic acid production profiling throughout acetification time (*t*) measured as **a** total acidity (*TA*) and **b** ethanol-acetic acid conversion. Errors represent standard deviation of fermentation triplicates. Created using Microsoft Office Professional Plus 2013

than fruit wines and in some cases this compound was absent from the analyzed samples. Acetaldehyde is an intermediary of ethanol oxidation to acetic acid which tends to accumulate in low oxygen conditions (Ribéreau-Gayon et al. 2006). Thus, considering ethanol-acetic acid conversion there was no accumulation of this major volatile and its concentration decreased. This decrease was also observed for higher alcohols 3-methyl-1-butanol, 2-methyl-1-butanol and methanol, previously correlated with unspecific oxidation by acetic acid bacteria (Ubeda et al. 2011). Regarding esters, a lower concentration of ethyl acetate was observed in fruit vinegars. Ethyl ester hydrolysis phenomena has been previously correlated with active ethanol consumption during acetic acid bacteria metabolism (Callejón et al. 2009). Methyl acetate concentration increased for orange and mango acetifications, which can be expected taking into account the correlation between methyl ester formation and methanol content in acidic conditions (Morales et al. 2002). Diethyl succinate concentration was higher, which can be a direct result of the strain or acetification conditions used (Callejón et al. 2008). Furthermore, some compounds previously quantified in the fruit wines were not found in the fruit vinegars. Such is the case of 2,3-butanediol in its *levo* and *meso* forms, which is believed to have been converted to acetoin during the acetification, identified in the minor compound analysis and coherent with the oxidation–reduction balance reported in previous works (Ribéreau-Gayon et al. 2006).

Minor volatile compounds

Fruit vinegars presented distinctive compositions of minor volatile compounds, (Table 1). Volatile fatty acids were found in all four fruit vinegars, which can be expected when taking into account the ability of

Table 1 Volatile composition, with correspondent mean concentration (*C*) of banana, orange, mango and cherry vinegars and fruit wines*, along with the corresponding sensory descriptors and their reported perception thresholds (*PT*). * Adapted from Coelho et al. (2015)

	Banana		Orange		Mango		Cherry		Descriptors	
	C/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*PT*/(μg L^{-1})	
	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar		
Minor volatiles										
Alcohols										
3-Ethoxy-1-propanol	403.8 ± 145.8	66 ± 42	217.6 ± 56.5	103 ± 13.8	294.3 ± 75.4	84 ± 44	68 ± 5.0	35 ± 46	50,000[b] [1]	
1-Octanol	–	–	1052.5 ± 117.6	–	–	–	–		10,000 [1][b]	Coconut, nuts, oily [2]
Furfuryl alcohol	–	–	–	–	161.4 ± 43.9	–	–	–	15,000 [3][a]	Hay, moldy [3]
Benzyl alcohol	–	–	56.1 ± 17.1	–	17.4 ± 3.7	–	382.0 ± 31.5	546 ± 353	200,000[a] [4]	Almonds, bitter [2]
1-Dodecanol		–		–		–		47 ± 19		
Esters										
Isobutyl acetate	–	–	–	–	342.1 ± 46.3	–	59.2 ± 1.4	–	1605 [5][a]	Banana, fruity, sweet [2]
Ethyl butyrate	–	299 ± 42.9	121.4 ± 0.6	–	364.5 ± 115.3	–	52.3 ± 9.7	–	20[b] [1], [6]	Fruity [7], papaya, sweet, butter, apple [2]
3-Methylbutyl acetate	3762.4 ± 1460.0	–	293.0 ± 61.8	–	2674.0 ± 879.1	–	1034.4 ± 16.1	–	30 [6], [1][b]	Banana, apple, solvent [2]
Ethyl hexanoate	911.8 ± 400.0	–	154.4 ± 45.6	–	413.6 ± 99.4	–	122.4 ± 8.0	–	14 [8][a]	Apple, fruity, aniseed, sweet [4]
Z-3-hexenyl acetate	–	–	–	–	–	–	14.5 ± 0.3	–	–	–
Ethyl octanoate	465.5 ± 160.3	–	127.4 ± 35.9	–	95.0 ± 13.2	–	42.6 ± 7.4	–	5 [8][a]	Apple, sweet, fruity [2]
Ethyl 3-hydroxybutyrate	45.3 ± 15.2	16 ± 7.0	9.2 ± 0.2	–	319.1 ± 50.0	158 ± 57.8	4.1 ± 0.6	–	20,000[a] [4]	

Table 1 continued

	Banana		Orange		Mango		Cherry		Descriptors	
	C/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*PT*/(μg L^{-1})	
	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar		
Ethyl decanoate	273.4 ± 134.3	–	38.9 ± 11.0	–	29.4 ± 14.2	–	16.6 ± 2.0	–	200 [8][a]	Fatty acid, fruity, apple, solvent [2]
Benzyl acetate	–	–	–	–	–	–	35.7 ± 3.0	14 ± 4.3		
2-Phenylethyl acetate	659.4 ± 203.5	–	296.3 ± 81.3	–	–	99 ± 7.4	98.0 ± 9.3	–	250[b] [6]	Roses, honey, apple, sweet [2]
Monoterpenic alcohols										
Linalool	–	–	6725.1 ± 1560	2541 ± 298.7	44.3 ± 16.4	–	38.6 ± 5.6	–	25.2[a] [8]	Aniseed, terpene [2], lemon [9]
Isopulegol I	–	–	183.5 ± 39.7	23 ± 1.5	–	–	–	–		
Fenchol	–	–	–	–	41.7 ± 6.0	–	–	–	50 [10][c]	Muddy [11]
Terpinen-4-ol		–	12,403.5 ± 3146.1	7785 ± 324.2	91.3 ± 20.9	–	14.4 ± 5.8	–		
Myrcenol	–	–	–	–	35.0 ± 2.8	–	–	–		
Borneol	–	–	–	–	53.5 ± 15.0	–	–	–		
α-Terpineol		–	3682.7 ± 983.9	2720 ± 97.47	1036.0 ± 275.3	–	11.8 ± 3.7	–	250[a] [8]	Pine, terpene [4]
β-Citronellol		–	306.6 ± 80.7	196 ± 7.77		–	9.3 ± 1.6	–	100[b] [1]	Citronella [12]
Nerol		–	279.9 ± 32.2	128 ± 16.5		–	7.5 ± 2.1	–	400–500[c] [13]	Lime, floral-hyacinth, roses [4]
Geraniol			241.1 ± 63.9				13.5 ± 1.3			
Monoterpenic oxides and diols										
trans-furan linalool oxide					92.9 ± 10.7					
cis-furan linalool oxide			93.3 ± 20.0		70.0 ± 22.4					
8-Hydroxy-6,7-dihydrolinalool			168.1 ± 54.5							
E-8-hydroxylinalool		131.7 ± 30.7	261.4 ± 99.2				11.4 ± 1.1			
Z-8-dihydroxylinalool		–		139 ± 11.1		–	14.3 ± 2.1	–		

Table 1 continued

	Banana		Orange		Mango		Cherry		Descriptors	
	C/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*PT*/(μg L^{-1})	
	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar		
C_{13}-norisoprenoids										
3-Hydroxy-β-damascone		–		–		–	50.8 ± 4.2	44 ± 8.5		
3-Hydroxy-7,8-dihydro-α-ionone							12.2 ± 1.8			
3-Oxo-α-ionol	30.1 ± 16.7	–	506.5 ± 156.1	181 ± 25.0	40.8 ± 12.2	–	664.7 ± 75.9	690 ± 155		
3-Oxo-7,8-dihydro-α-ionol	63.1 ± 35.9		280.7 ± 84.3		154.7 ± 39.6		45.0 ± 6.0			
Volatile phenols										
Eugenol	8204.6 ± 3027.4	1417 ± 189.5	236.2 ± 76.1	118 ± 5.43		–	224.6 ± 39.0	271 ± 52.7	6 [8]; 15 [3][a]	Clove-like [7] [3]
4-Vinylguaiacol	188.3 ± 48.7	18 ± 9.7	2890.2 ± 976.7	1631 ± 90.63	329.8 ± 90.1	–	6.1 ± 0.4	–	130 [3]; 1100 [8][a]	Phenolic, bitter [2]; pharmaceutic-spicy [11]
4-Vinylphenol	–	–	636.8 ± 298.3	370 ± 26.1	23.1 ± 5.0	–	6.3 ± 0.9	–	180[a] [3]	Stramonium [3]; pharmaceutic [11]
Acetovanillone	85.9 ± 38.1		49.7 ± 21.8		–		18.2 ± 2.6		1000 [4][a]	
Zingerone	37.0 ± 15.9	–	282.3 ± 90.9	–	–	–	12.1 ± 4.4	11 ± 3.4		
Volatile fatty acids										
Propanoic acid	–	510 ± 240	32.6 ± 9.6	–	40.8 ± 15.2	260 ± 221	–	467 ± 225	8100 [14][b]	Vinegar [15]
Butanoic acid	408.3 ± 153.6	14 ± 5.4	77.9 ± 26.8	77 ± 7.8	687.9 ± 186.9	476 ± 192	7.0 ± 2.4	28 ± 16	173 [8][a]	Butter, cheesy, sweat [2]
2-Methylpropanoic acid	539.5 ± 188.6	898 ± 222	–	–	97.8 ± 18.8	559 ± 192	21.0 ± 2.6	443 ± 166	2300 [8][a]	Sweaty, bitter, vinegar [2]
Isovaleric acid		5345 ± 1022		4349 ± 460.7		8552 ± 3350		5863 ± 2438	33.4 [8]; 8 [16][a]	Cheesy, sweaty, old hops [2]
3-Methyl + 2-methylbutyric acids	727.8 ± 242.2		39.2 ± 9.7		241.8 ± 63.1		30.3 ± 3.3			

Table 1 continued

	Banana		Orange		Mango		Cherry		Descriptors	
	C/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*PT*/(μg L^{-1})	
	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar		
Hexanoic acid	1047.0 ± 389.9	323 ± 80	971.5 ± 259.4	856 ± 46.7	731.6 ± 147.5	378 ± 63.1	193.8 ± 21.7	–	420 [8][a]	Fatty acid, oily, sweaty [2]; green [12]
Octanoic acid	2090.8 ± 797.0	129 ± 15.8	1047.1 ± 324.6	1660 ± 171.2	918.3 ± 219.2	344 ± 66.0	543.5 ± 56.5	338 ± 67.3	500 [8][a]	Fatty acid, oily, sweaty [2]
Decanoic acid	545.1 ± 174.4		–		21.9 ± 5.6		97.1 ± 9.7			
Lactones										
Methoxyfuraneol					48.1 ± 10.1					
Furaneol		–		–	1180.1 ± 281.5	383.93 ± 132.67		–	37 [16][a]	Caramel [7]
γ-Decalactone							22.9 ± 3.8		1000 [1][b]	
Sulfur compounds										
2-Methyltetrahydrothiophen-3-one							19.8 ± 2.3			
2-(Methylthio)ethanol	–	–	–	–	50.5 ± 8.2	–	–	–		
Methionol	65.0 ± 20.6	–	–	–	510.3 ± 115.9	55 ± 81	4.1 ± 0.7	–	1000 [8][a]	Cooked potato-like [7]
Carbonyl compounds										
Acetoin		11,752 ± 3468.6		7062 ± 1619		5985 ± 3229		3828 ± 1192	152,600 [14]; 30,000 [1][b]	Fruity, moldy, woody [2]
Benzaldehyde		15 ± 6.4		–		–	364.0 ± 48.3	28 ± 10	5000 [1][b]	Almond [14]
6-Methyl-5-hepten-2-one							364.0 ± 48.3			
Major volatiles										
Acetaldehyde	5260 ± 710	–	13,300 ± 1380	3435 ± 209.7	20,800 ± 2510	–	7430 ± 1180	–	25 [7][c]	Fresh, green [7]
Methyl acetate	3380 ± 270	–	6840 ± 1050	7039 ± 3251	6890 ± 1350	16,539 ± 1833	–	–		
Ethyl acetate	66,100 ± 38,000	–	13,300 ± 480	6906 ± 2152	39,500 ± 2560	8522 ± 3155	18,400 ± 1040	–	7500 [6][b]	Solvent, fruity [2]
Methanol	42,400 ± 11,700	23,000 ± 4146	213,000 ± 40,200	41,911 ± 2058	109,000 ± 31,400	46,013 ± 13,519	16,800 ± 6070	25,564 ± 4147		

Table 1 continued

	Banana		Orange		Mango		Cherry		Descriptors	
	C/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*C*/(μg L^{-1})		*PT*/(μg L^{-1})	
	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar	Wine*	Vinegar		
1-Propanol	193,000 ± 50,000	–	116,000 ± 3670	2865 ± 374.5	87,400 ± 9050	–	236,000 ± 29,300	–		
2-Methyl-1-propanol	63,700 ± 19,100	5657 ± 3874	15,300 ± 1410	2641 ± 302.4	45,000 ± 1340	3240 ± 450.1	24,500 ± 1650	–	550 [7][c]	Malty [7]
2-Methyl-1-butanol	24,900 ± 7260	4035 ± 924.3	18,700 ± 810	3443 ± 473.5	43,100 ± 2290	6557 ± 2171	14,900 ± 1580	–	1200 [7][c]	Malty [7]
3-Methyl-1-butanol	100,000 ± 26,300	5876 ± 4682	69,700 ± 1270	3372 ± 675.6	164,000 ± 11,500	3937 ± 1330	120,000 ± 1160	–	220 [7][c]	Malty [7]
2,3-Butanediol, levo	365,000 ± 79,500	–	208,000 ± 26,000	–	245,000 ± 81,800	–	305,000 ± 63,400	–		
2,3-Butanediol, meso	119,000 ± 27,300	–	65,000 ± 11,700	–	93,400 ± 31,800	–	87,600 ± 20,700	–		
Diethyl succinate	1420 ± 420	16,407 ± 2027	–	9074 ± 1461	–	9097 ± 1226	–	11,918 ± 1156		

Errors represent standard deviation of fermentation triplicates

[1] Moreno et al. (2005), [2] Meilgaard (1975), [3] Boidron et al. (1988), [4] Gómez-Míguez et al. (2007), [5] Ferreira et al. (2002), [6] Guth (1997), [7] Czerny et al. (2008), [8] Ferreira et al. (2000), [9] Escudero et al. (2004), [10] La Guerche et al. (2006), [11] Boutou and Chatonnet (2007), [12] Ribéreau-Gayon et al. (2006), [13] Ribéreau-Gayon et al. (1975), [14] Étievant (1991), [15] Siebert et al. (2005), [16] Kotseridis and Baumes (2000)

[a]Threshold in model solution, [b]Threshold in hydroalcoholic solution, [c]Threshold in water, – Not detected

Acetobacter to oxidize other organic compounds beyond ethanol (Sengun and Karabiyikli 2011). Isovaleric acid was the main volatile fatty acid found in fruit vinegars. Its formation was expected from the metabolism of 3-methyl-1-butanol by acetic acid bacteria (Ubeda et al. 2011). Acetoin was also found in all fruit vinegars at high proportions, which was expected when taking into account the oxidative balance of 2,3-butanediol previously discussed. Highlighting distinguishing features in minor volatile compounds, orange vinegar presented distinctive content of monoterpenic alcohols with descriptors coherent with orange aroma. For instance linalool, α-terpineol and β-citronellol were found above perception thresholds, which correlated with orange and citric descriptors. Despite lacking for minor volatiles typically associated with cherry or red fruits sensory descriptors, cherry vinegar presented distinctive composition of C_{13}-norisoprenoids and benzaldehyde which have been previously correlated with cherry aroma (Coelho et al. 2015). Banana vinegar presented higher content of esters, with ethyl butyrate above the perception threshold, associated with fruity aroma descriptors. Regarding mango, furaneol, a lactone associated with mango sensory descriptors, was found relating with varietal aroma (Kulkarni et al. 2013). Overall minor volatile concentration and diversity in fruit vinegars was lower than in the corresponding fruit wines. Esters, alcohols and monoterpenic alcohols content and diversity were overall lower, and minor volatile fatty acids content was higher, potentially caused by previously discussed phenomena related to *Acetobacter* metabolism.

Antioxidant activity

FRAP analysis, presented in Fig. 2 allowed an insight on fruit vinegars antioxidant activity and their comparison with commercial cider vinegar.

Cherry and orange vinegars demonstrated higher antioxidant activity, consistent with the previously reported for the corresponding fruits (Fu et al. 2011) and fruit wines (Coelho et al. 2015). Moreover, it can be seen that antioxidant activity values found in fruit vinegars were similar to the naturally occurring in the corresponding fruits, which can be due to the utilization of fruit concentrates. Overall, antioxidant activity in the reported fruit vinegars was between 8 and 40 folds higher than traditional cider vinegar. The utilization of alternative fruits in their concentrated form, allowed the production of antioxidant enhanced vinegars, maintaining functionality and adding value to vinegar products.

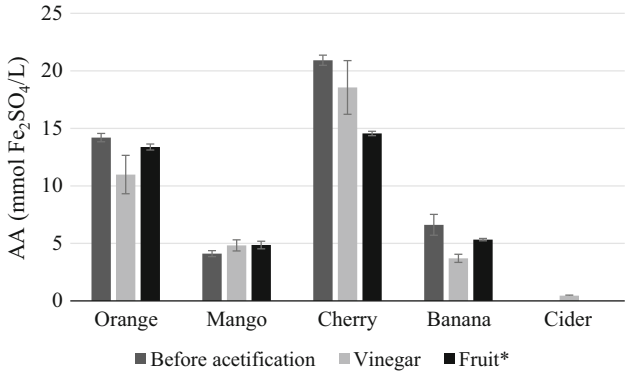

Fig. 2 Antioxidant activity (*AA*), measured by FRAP, before acetic fermentation and in fruit vinegars, compared to commercial cider vinegar and the one reported for the corresponding fruits. Errors represent standard deviation of fermentation triplicates. *Adapted from Fu et al. (2011). Created using Microsoft Office Professional Plus 2013

Conclusion

Four fruit vinegars were produced and characterized from industrial whole fruit concentrates. Acetification of fruit wines was feasible in the studied conditions and fruit vinegars acidity was within the required parameters. Volatile compounds analysis allowed an insight of *Acetobacter* metabolism on aroma composition. Despite the transformations observed, fruit vinegars presented minor volatiles coherent with varietal aroma. Antioxidant activity was found in all four fruit vinegars at values close to the ones reported for the given fruits, and remarkably higher than the one found in cider vinegar. The already demonstrated importance of antioxidant rich foods in human nutrition, which inhibit the harmful activity of free radicals naturally generated during oxidative metabolism, reinforces the value of vinegar production from antioxidant rich raw materials. Therefore, the combination of fruit antioxidant content with vinegar's nutritional benefits strengthens the viability of fruit vinegar production from fruit concentrates for the preservation, delivery and enhancement of functional features.

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