





UVA Induced Quality Deterioration of Ponkan Mandarin Juice

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Abstract: Ponkan mandarin is a promising variety of citrus fruit for juice production. However, there is little knowledge in shelf-stability of Ponkan juice under normal sun lighting. In this study, Ponkan juice was investigated for the changes of quality under the most common powerful irradiation of sunlight, ultraviolet A (UVA). Properties related to taste, color, nutritive values, characteristic mandarin aroma, and volatile sulfuric off-flavor were analyzed to make a comprehensive evaluation. The results showed that after 50 days UVA radiation through PET bottles at 25°C, juice acidity, total soluble solid content, chromaticity values, vitamin C and B2 content decreased significantly, and the characteristic mandarin aroma weakened. In addition, 10 more volatile sulfur compounds introducing distinctly off-putting smell were detected than the fresh juice. UVA is responsible for the accelerated deterioration of Ponkan juice quality and should be properly shielded.

1 INTRODUCTION


Mandarin (*Citrus reticulata* Blanco) is a variety of citrus whose fruits are thin-skinned and easy-peeling. The most popular cultivars include Ponkan, Satsuma, Tangerine and Clementine. According to a report from the United States department of agriculture, the global production of mandarin will reach 30 million tons per year (USDA 2019). Almost all mandarin production is sold as fresh fruit. Due to the saturation of the fresh fruit market and the changes in consumer preferences, an increase in mandarin juice production is to be anticipated.


Food products placed on outdoor market shelves are exposed to sun light. It is known that light, especially ultraviolet, can accelerate the oxidation of fat, degradation of ascorbic acid, browning of color, and formation of off-flavor (Conrad 2005, Zhang 2015, Hashizume 2006). Riboflavin-promoted formation of reactive oxygen species, such as


superoxide anion, single oxygen, hydroxyl radical and hydrogen peroxide, can result in the degradation of amino acids, lipids, carbohydrates, and vitamin (Grant 2017). In the presence of light and oxygen, off-flavor can be formed in the orange juice due to the lipid peroxidation (Fan 2004). Light also increases the off-flavored volatiles in cloudy apple juice such as 1-octen-3-one pentanal, 2-methyl-1-penten-3-one, hexanal, (E)-2-heptenal, 6-methyl-5-hepten-2-one, and (E)-2-octenal (Hashizume 2006).


Volatile sulfur compounds (VSCs) are known to be responsible for heated juice off-flavor (Cheng 2020). They introduce a variety of odor characteristics: rotten eggs, potato, cabbage, meat, coffee, and onion (I-Min 2011). VSCs are degradation products of amino acid precursors like methionine, S-methyl methionine, cysteine and so on (Gonda 2013, Lee 2014). In white wines, UV-visible light can increase the amount of volatile methanethiol and dimethyl disulfide, too, resulting in the sunlight flavor (Grant 2017).

Juice quality is a comprehensive combination of color, flavor, nutritive value, and other physical-

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chemical properties. Mandarin juice had been less studied for its quality. The objective of this study was to investigate changes of several commercially important properties of Ponkan mandarin juice such as chromaticity, vitamin C and B2, volatile organic and sulfur compounds after an ultraviolet-A (UVA) radiated shelf-life, and evaluate the resulting deteriorative effect on the juice quality.

2 MATERIALS AND METHODS

2.1 Sample Preparation

Fresh mature Ponkan fruits were purchased from a local market in Chongqing, China. Fruits were hand-squeezed and the released juice was pasteurized for 30s at 98°C and hot-filled into sterile 200 mL polyethylene terephthalate (PET) bottles. Bottles were sealed and cooled immediately using an ice bath to reach the ambient temperature. Bottles were exposed separately in the dark (control) or under UVA (360nm, 25μW/cm²) radiation at 25°C for a 50-day shelf-life study.

2.2 Vitamin C Determination

A 2,6-dichloro indophenol method was used to determine the content of ascorbic acid (Harris 1942).

2.3 Measurement of Chromaticity

L*, A* and B* were measured respectively by using a Juice chromometer, where L* value indicates whiteness, A* for red/green color, and B* for yellow/blue color (Min 2002).

2.4 Extraction and HPLC Analysis of Riboflavin

A C18 solid-phase extraction procedure was adopted with modifications from Blanco-Gomis (Gomis 1994). Fifteen milliliters of juice were acidified with 2 mL of 1M H₂SO₄ at 100°C for 30 min. It was cooled down and adjusted to pH5-6. A 15 mL mixture was centrifuged at 13362 g for 15 min. The supernatant passed through a C18 cartridge that had been previously conditioned by 5 mL methanol and washed with 10 mL of water. Riboflavin was eluted using 5 mL of methanol. Solvent was evaporated under nitrogen at 35°C. The extract was then redissolved in 0.4ml of aqueous methanol solution

(50/50, v/v) and membrane filtered before an HPLC injection.

An Agilent C18 column (150×4.6 mm, 5μm) connected to a 1260 LC system was used to analyze riboflavin. Separation was based on an isocratic method using methanol-water (35:65, v/v) as the solvent. The flow rate was 0.7 mL/min, and the injection volume was 5 μL. Fluorescence detection was monitored at an emission wavelength of 522 nm.

2.5 Static Headspace Solid-phase Micro-extraction

A 20 mL vial containing 5 mL of juice was equilibrated at 40°C for 20 min. A 2 cm-long fiber coated with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) was exposed in the headspace for 30min. The extracted juice volatiles were desorbed for 5 min at 200°C in GC inlet port.

2.6 Gas Chromatography-Mass Spectrometry/Pulsed Flame Photometric Detection (GC-MS/PFPD)

Volatiles were analyzed using an Agilent-7890B GC equipped with a 5977B MS detector coupled to a 5380 PFPD (OI Analytical). Separation was on an RTX-Wax column (60 m×0.25 mm id×0.25 μm). The temperature program was set as the following gradient: 35°C for 6min; linearly elevated to 203°C at a rate of 7°C/min and held for 10 min. Electron impact (EI) voltage was set at 70 ev, and the m/z range was set between 44 and 300 amu. For VSCs detection, the temperature of PFPD was set at 250°C. Identification of compounds was confirmed by matching the TIC spectra to the mass spectral library (W10N14), comparing with authentic standards, and/or checking their linear retention index (LRI). Quantitation of characteristic volatiles was applied by using a cyclohexanone internal standard method.

2.7 Sensory Evaluation

Ten well-trained assessors (6 females and 4 males, ages between 22 and 40 years) participated in sensory analysis of Ponkan juice. Sensory evaluation was conducted at room temperature under clean air conditions. Evaluation criteria are shown in Table 1 as below.

Table 1: Sensory evaluation criteria for Ponkan juice.

Item	Score	Criteria
Appearance and Defects	20	No stratification, flocculation & obvious defects, 20 points; a small amount of flocculation, stratification & impurities, 12-19 points; serious flocculation, stratification & impurities, 0-11 points.
Flavor	50	Showing citrus characteristic aroma, without any bitterness, astringency, and off-flavor, 50 points; insufficient aroma, slightly more sour or sweeter, no bitter, astringent, but with a hint of cooked smell, 35-49 points; poor aroma, too sour or sweet, with a slight bitterness and cooked smell, 18-34 points; no characteristic aroma, very sour, bitter and serious smelly, 0-17 points.
Color	30	Typical bright mandarin color, stable and homogenous, 18-30 points; dim and uniform, 14-17 points; dark and less uniform, 10-13 points; colorless and nonuniform, 0-9 points.

2.8 Data Analysis

All analyses were performed in triplicate. Analysis of variance were performed using SPSS 22.

3 RESULTS AND DISCUSSIONS

3.1 Changes in Physical and Chemical Indices

After 50 days UVA radiation, results of the essential physical and chemical properties relating to Ponkan juice quality are shown in Figure 1. Juice stored in dark condition is compared as a control. Data with significant differences are labelled with different letters. The figure shows that juice acidity, total soluble solid content, color (including brightness L*, redness a*, and yellow b*), vitamin C content, and vitamin B2 content were all significantly lower in UVA radiated juice than those in dark stored and fresh juices. Particularly, over 98% of riboflavin (VB2) had been lost. They were likely to participate in the formation of reactive oxygen species and responsible for the degradation of VC which decreased by about 70%.

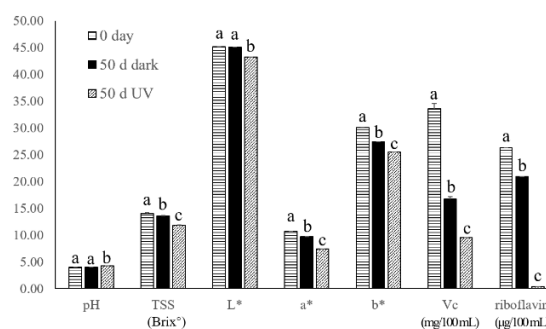


Figure 1: Comparison of major physical and chemical properties among three juice samples.

Notes: TSS, total soluble solids; L*, a*, b*, three dimensions of chromaticity; a-c, significant differences.

3.2 Characteristic Volatile Flavor Components

In addition to taste, color and nutritional properties, characteristic mandarin aroma is another important trait of Ponkan juice. The characteristic aroma compounds in fresh juice and juices that had been stored for 50 days in dark condition and under UVA lighting were analyzed using GC-MS. The odor activity value (OAV), which is a quotient of the sample concentration divided by the threshold concentration, were calculated to describe the aroma/flavor intensity of each compound. The results of compound identification, odor description and OAVs of the three samples are shown in Table 2. There were significant differences of the intensities of various aroma attributes among samples. For example, OAVs of off-flavor compounds such as α -pinene (piny), β -myrcene (moldy), perillaldehyde (solvency), terpinen-4-ol (woody), thymol (medicinal), and carvone (caraway) have greatly increased after 50 d UVA irradiation. Accumulation of these compounds would destruct the aroma balance of the Ponkan juice. Only slight increases were detected in the juice sample stored in dark. In addition, some typically good aroma attributes such as citrusy, green, lemony, floral, mint, and fruity have decreased considering their total aroma intensity.

Table 2: Characteristic aroma identification and flavor intensity among three Ponkan juice samples.

No.	Compounds	Odor	OAV		
			0 d	50 d dark	50 d UV
1	α -pinene	piny	59	100	124
2	camphene	camphor	16	2	2
3	β -myrcene	moldy	45	63	82
4	d-limonene	citrusy	1430	860	1060
5	p-cymene	citrusy	51	71	173
6	γ -terpinene	citrusy	43	34	23
7	terpinolene	piny	26	21	17
8	hexanal	green	16	7	6
9	nonanal	lemony	6	4	2
10	perillaldehyde	solveny	4	5	7
11	1-octanol	citrusy	1	1	-
12	linalool	floral	860	370	330
13	cis-p-2-menthen-1-ol	mint	16	2	2
14	fenchol	unpleasant	-	-	2
15	terpinen-4-ol	woody	2	5	5
16	α -terpineol	floral	4	15	23
17	citronellol	fruity	9	19	24
18	carveol	caraway	0	0	1
19	thymol	medicinal	2	2	8
20	carvone	caraway	2	4	120
21	ethyl 2-methyl propanoate	fruity	30	36	43
22	butanoic acid, ethyl ester	fruity	8	2	2
23	ethyl 2-methyl butanoate	fruity	1720	1790	340

Notes: OAV, odor activity value.

3.3 Volatile Sulfur Compounds

Volatile sulfur compounds (VSCs) are known to be responsible for a variety of bad smell characteristics. In this study we found both the number of compounds and their concentrations were increased after 50 d storage. As shown in Figure 2, fresh Ponkan juice only contain small amount of hydrogen sulfide (H_2S), methanethiol ($MeSH$), dimethyl sulfide (DMS), and ethyl (methylthio)acetate (EMA). Additional VSCs were found in the 50 days stored juice, such as S-Methyl thioacetate, (MTA), dimethyl disulfide, (DMDS), 2-methylthiophene (2-MT), 3-methylthiophene (3-MT), dimethyl trisulfide (DMTS), and methional. The content of DMS increased, too. After 50 days storage under UVA radiation, more amount of DMS, DMDS, 2-MT, 3-MT, DMTS and methional were observed. Carbon disulfide (CS_2) and three unknown VSCs were newly detected. The odors of DMS, DMDS, DMTS,

methional, and CS_2 have been described as cabbage, onion, garlic, cooked potato, and solveny, respectively. Increases of these specific sulfur off-flavors in addition with other unknown VSCs would definitely undermine the comprehensive flavor of Ponkan juice.

3.4 Deterioration of Juice Overall Quality

The overall apparent sensory quality scoring by assessors showed a consent to above analytical results. In the item of Appearance and Defects, scores for fresh juice, 50 days in dark and 50 days under UV were 18, 17 and 15. Scores of Flavor were 40, 37 and 30, respectively. Color scores were 18, 18 and 17, respectively. The total scores were 76 (fresh), 72 (dark) and 62 (UVA).

4 CONCLUSIONS

In this study we have shown that the overall quality of Ponkan mandarin juice deteriorated after being placed on shelf under UVA radiation at an ambient temperature (25°C) for 50 days. The control, same juice placed in dark, showed a much better quality close to the fresh juice. These results demonstrate that UVA, the major UV irradiation in our everyday life, should be screened so that to protect juices from quality deterioration.

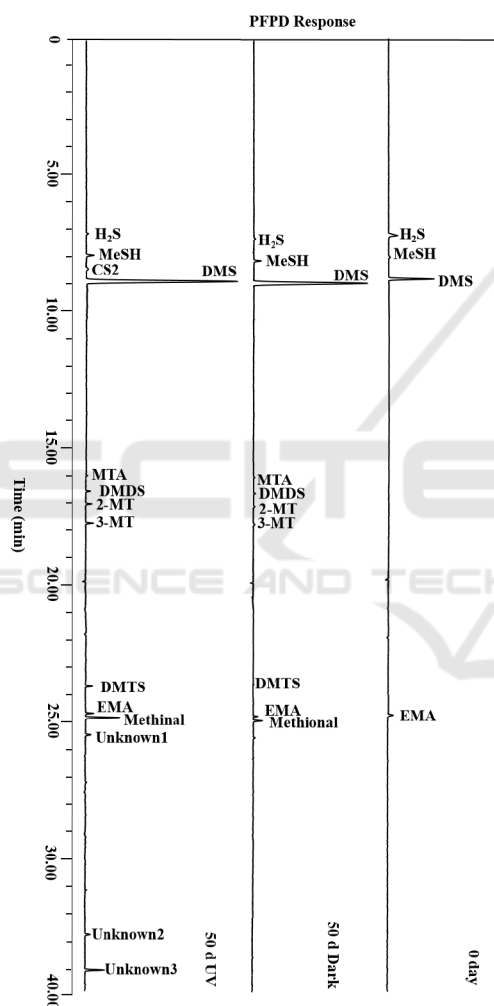


Figure 2: VSCs chromatogram detected using PFPD.

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REFERENCES

- Cheng, Y. J., et al. (2020) Methanethiol, an off-flavor produced from the thermal treatment of mandarin juices: a study of citrus sulfur volatiles. *J. Agric. Food Chem.*, 68(4): 1030-1037.
- Citrus: World markets and trade. <https://apps.fas.usda.gov/psdonline/circulars/citrus.pdf> (accessed Sep 2019).
- Conrad, K. R., et al. (2005) Influence of PET and PET/PEN blend packaging on ascorbic acid and color in juices exposed to fluorescent and UV light. *J. Food Sci.*, 70(1): 19-25.
- Fan, X. (2004) Involvement of volatile sulfur compounds in ionizing radiation-induced off-odor of fresh orange juice. *J. Food Sci.*, 69(8): 593-598.
- Gomis, D. B., et al. (1994). High-performance liquid chromatographic determination of cymiazole in honey with UV and electrochemical detection. *Chromatographia*, 39(9): 602-606.
- Gonda, I., et al. (2013) Catabolism of L-methionine in the formation of sulfur and other volatiles in melon (*Cucumis melo* L.) fruit. *Plant J.*, 74(3): 458-472.
- Grant, P. P., et al. (2017) Light-induced changes in bottled white wine and underlying photochemical mechanisms. *Crit. Rev. Food Sci. Nutri.*, 57(4): 743-754.
- Harris, L. J. & Olliver, R. J. (1942) Vitamin methods 3. The reliability of the method for estimating vitamin C by titration against 2,6-dichlorophenolindophenol. 1. Control tests with plant tissues. *Biochem. J.*, 36: 155-182.
- Hashizume, M., et al. (2006) Light-induced off-flavour in cloudy apple juice. *Dev. Food Sci.*, 43(06): 273-276.
- I-Min, T. & Mina, R.M. (2011) Volatile Sulfur Compounds in Food. In *Understanding Aroma Impact of Four Important Volatile Sulfur Compounds in Oregon Pinot Noir Wine*, Qian, M.C., Fan, X., and Mahattanatawee, K. (Eds.), Am. Chem. Soc., Washington. pp. 279-312.
- Lee, H. R., et al. (2014) Digestive recovery of sulfur-methyl-L-methionine and its bioaccessibility in Kimchi cabbages using a simulated in vitro digestion model system. *J. Sci. Food Agric.*, 94(1): 109-112.
- Min, J. S., et al. (2002) Real Effect of pH on CIE L*, a* and b* of Loins during 24 h Chilling of Beef Carcasses. *Asian Austral. J. Anim.*, 15: 2.
- Zhang, L. C. et al. (2015) Regulation of ascorbic acid metabolism by blue LED light irradiation in citrus juice sacs. *Plant Sci.*, 233: 134-142.