Characterisation of volatile compounds of pineapple peel wine

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Abstract. An analytical program based on the headspace solid phase microextraction (HS-SPME) method combined with gas chromatography – mass spectrometry (GC-MS) was developed to extract and analysis profiling of volatiles from pineapple peel wine. In total, 57 volatile compounds were detected on the basis of the MS information and RI, including 25 esters, 9 alcohols, 8 acids, 7 phenolic compounds, 6 aldehydes and ketones, 1 terpene and 1 lactone, respectively. The types of esters are the most in various aroma substances, and the content of alcohols is the largest. Phenethyl alcohol, 3-methyl-1-butanol, 2-methyl-1-butanol, 2,3-Butanediol and 2-Methoxy-4-vinylphenol were the major constituents.

1 Introduction

Pineapple (*Ananas comosus* L. [Merr.]), one of the most popular subtropical fruits, has plentiful nutrition and unique flavor. Pineapple is abundant in micronutrients and antioxidants, for instance, vitamin C, polyphenols, flavonoids and phytochemicals^[1]. In addition, it also contains sufficient amounts of minerals, especially potassium and calcium. Pineapple consumed in fresh and processed forms, widely processed into canned food, beverages, and food supplements. Simultaneously, a large number of peel, representing 29-40% (w/w) of the whole pineapple weight, is discarded in processing industry^[2]. However, abundant evidence proves pineapple peel contains crucial bioactive substance and aroma compounds^[3-4]. The development of pineapple peel wine can not only help reduce waste, but also meet the strong public demand for novel quality products. Compare with the pulp, pineapple peel might contribute to the wine with more plentiful and unique flavors. Currently, little research on volatile compounds in pineapple peel wine is reported. Consequently, the purpose of this study was to investigate the characterisation of volatiles in pineapple peel wine to develop novel alcoholic beverage.

2 Materials and Methods

2.1 Chemicals and reagents

Yellow mauritius pineapple were obtained from Nanpai Farms (Zhanjiang, Guangdong Province). Pectinase and cellulase were purchased from Shanghai Yuanye Biological Technology Co., Ltd.

2.2 Wine making

The pineapple peel was placed into fermentor containing distilled water at a ratio of 1.5:1 and then subjected to maceration treatment at 70°C for 30 min. Afterwards, the mixture was cooled to 45 ± 5°C and subjected to enzymatic hydrolysis, using pectinase and cellulase as catalysis. The must, adjusted the sugar content to 20°Brix by sucrose solution, was fermented by Yeast QA23 on the concentration of 200 mg/L at 18°C. Sodium metabisulfite was added up to a concentration of 60 mg/L to inhibit the growth of bacteria. Fermentation termination was determined when the sugar content remained keep stable.

2.3 GC–MS analysis of the volatile compounds in the wine

The sample was analyzed using HS-SPME–GCMS as previously reported, with modifications. 1 mL of wine sample was added into glass bottles containing 0.5 g of NaCl. The fiber used for the extraction of the volatiles was the DVB/CAR/PDMS, and the procedure was carried out using the auto-sampler. The SPME fiber was extracted at 45°C for 15 min and then stabilized for 5 min. Subsequently, the fiber was inserted into the injection port of the GC device for thermal desorption. The thermal adsorption of the compounds in the fiber was fulfilled in a splitless manner at 250 °C for 5 min. The analyses were via an GC-MS-QP2010 Plus, and a Rtx-5ms capillary column was used. The flow rate of the carrier gas was 1.08 mL/min. The temperatures of the interface and the ion ionization source were 250 °C and 230 °C, severally. The sequence of the GC oven program was as follows: 45°C for 2 minutes, at a rate of 5°C/min

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to 180°C for 27 minutes, and then at a rate of 20°C/min to 240°C. The ionization voltage was 70 eV, and data acquisition was carried out within a scan range of m/z 35 to 500. The identification of the volatiles was fulfilled using mass spectra and retention indices, and the area normalization method was used to quantitate^[5].

3 Results and discussion

3.1 HS-SPME-GC-MS analysis of volatile compounds in wine sample

HS-SPME-GC-MS was applied to detect volatile components of pineapple wine in this study. Fig. 1. showed the HS-SPME-GC-MS total ion current chromatograms of the sample. Results obtained showed that a total of 57 typical volatiles were detected on the basis of the MS information and RI, including 25 esters, 9 alcohols, 8 acids, 7 phenolic compounds, 6 aldehydes and ketones, 1 terpene and 1 lactone.

Fig. 1. Total Ion Chromatograms of Aromatic Components in Pineapple Peel Wine.

3.2 Analysis of esters in pineapple peel wine

Esters, major volatile components, are an essential part of the aroma skeleton in wines. The volatiles are primarily formed by fruit and alcohol fermentation, contributing to the wine with desirable and fruity sensory properties, including banana, strawberry and green apple^[6]. As can be seen in table 1, the total relative content of esters in pineapple peel wine was 5.86%. A total of 25 esters represented the largest group, among them 11 fatty acid ethyl esters, 6 higher alcohol acetates, 4 aromatic esters, 3 fatty acid methyl esters and propyl enanthate. Some important esters, suggesting that a more intense fruity aroma could be perceived in such a wine. Ethyl lactate, associated with fruit and cream odors, had the highest content among the various esters, suggesting a rum aroma might be perceived in this wine, followed by phenethyl acetate, contributing to the wine with rich rose aroma and strawberry-like aroma. Moreover, a total of 4 sulfur-containing esters were identified in pineapple peel wine, i.e., methyl 3-methylthiopropionate, ethyl 3-methylthiopropionate, 3-(methylthio)propyl acetate and sulfurous acid, 2-ethylhexyl nonyl este, separately.

3.3 Analysis of Alcohols in pineapple peel wine

Alcohols, playing a significant role in the fragrance component, are metabolites formed by yeast through sugar catabolism or decarboxylation reaction and deamination of amino acids^[7]. Such substances, set off the ester aroma and promote the coordination of aromas, have a critical contribution on the aroma of fermented products. Alcohols had the highest concentration of all volatiles in our research, with a total relative content of 62.68 %. As shown in table 1, a total of 9 alcohols were detected in this study, namely 3-methyl-1-butano, 2-methyl-1-butano, 2,3-Butanediol, 1-pentanol, 3-methyl-, n-heptanol, 1-propanol, 3-(methylthio)-, 1-octanol, phenethyl alcohol and cedrol, respectively. Notably, phenylethyl alcohol had the highest concentration of all volatiles, with a relative content of 32.17%, which constitutes the main aroma substance of pineapple peel wine. It is a derivative of shikimic acid, with a delicate and delicate rose fragrance and rose fragrance. In addition, 3-methylthiopropanol, also known as pineapple alcohol, is found in fruits, beer, white wine, fruit wine and soy sauce. At low concentrations, it can give fruit wine the smell of onion and broth. 1-octanol has fat wax aroma, oily fruit aroma, grass aroma and rose smell.

3.4 Analysis of fatty acids in pineapple peel wine

Different concentration of fatty bring about different aroma sensory. Fatty acids was associated with creamy and cheese flavor in low concentration, while the volatiles provide astringent and rancid odors in high concentration, reacting with alcohols to form esters and make the aroma of wine more coordinated. Octanoic acid, having the highest signal intensities of total fatty acids, is usually oily, musty and rancid, but when its concentration is low, it has a pleasant cheese and fruity aroma.

3.5 Analysis of aldehydes and ketones in pineapple peel wine

Aldehydes and ketones, formed by alcohol oxidation, are the primary contributors to fruit aromas, providing a fruit flavor with strong fruity, fresh, and green leaves to fruit wines due to their low thresholds^[8]. However, these compounds are unstable and will be further oxidized to carboxylic acids, reducing their content^[9]. a total of 5 aldehydes were identified from the current sample, with a total relative content of 0.91%, i.e., nonanal, (e)-2-dodecenal, dodecanal, 2-undecenal and n-tetradecanal. Among them, dodecanal was associated with sweet floral and odor, suggesting a citrus aroma might be perceived in this wine. Furaneol, the only one compound belonging to the furans group, was detected from the experimental pineapple peel wine.

3.6 Analysis of phenolic compounds in pineapple peel wine

Phenolic compounds provide the aroma of similar drugs to fruit wine^[10]. a total of 7 aldehydes were identified in the pineapple pomace fruit wine, with a total relative content of 17.62%. Among them, 2-methoxy-4-vinylphenol is the phenolic substance with the highest content in the wine sample. It has a strong spice, clove and fermented aroma, with a smell of fried flowers. Moreover, 4-ethyl-2-methoxyphenol has a sweet and warm spice and herb-like aroma, eugenol has a strong lilac fragrance.

3.7 Analysis of terpenes in pineapple peel wine

Terpene compounds generally exist in the fruit in the form of glycosides. During fermentation, they form free and volatile substances under the action of acid or enzymatic hydrolysis, thereby associated with fruity and floral aromas, which are important varieties in fruit wines. The aroma threshold of those group is low, suggesting that it has a greater contribution to the aroma of fruit wine even at a lower concentration^[11]. The only one compound belonging to the terpene group were identified in this study, i.e., terpineol, responsible for clove aroma. In addition, 4-hexanolide, a lactone, was detected in pineapple peel pomace fruit wine, which has a mild and powerful coumarin-like aroma with a medicinal taste, and a coumarin and caramel-like taste.

Table 1. The identified volatile compounds of pineapple peel wine using HS-SPME-GC-MS.

Peak	RT (min)	Compound	Relative content /%
Esters			
1	4.2	Isobutyl acetate	0.03
2	5.1	Ethyl lactate	1.55
3	6.7	Isoamyl acetate	0.25
4	6.8	1-Butanol, 2-methyl-, acetate	0.04
5	9.2	Benzoic acid, 4-(1,3-dioxolan-2-yl)-, methyl ester	0.08
6	9.3	Ethyl Acetate	0.09
7	11.3	Methyl 3-methylthiopropionate	0.27
8	12.3	Pentanoic acid, 2-hydroxy-4-methyl-, ethyl ester	0.12
9	13.2	Heptanoic acid, propyl ester	0.1
10	13.6	Butanoic acid, 2-methyl-3-oxo-, methyl ester	0.02
11	13.7	Ethyl 3-Methylthiopropionate	0.54
12	14.4	3-(Methylthio)propyl acetate	0.02
13	16.7	Ethyl octanoate	0.06
14	18.1	Benzeneacetic acid, ethyl ester	0.06

15	18.5	2-Phenethyl acetate	1.34
16	22.4	Ethyl decanoate	0.12
17	23.8	Carbonic acid, ethyl pentyl ester	0.05
18	24.1	Dimethyl phthalate	0.02
19	27.5	Ethyl dodecanoate	0.17
20	30.0	Sulfurous acid, 2-ethylhexyl nonyl ester	0.04
21	30.6	Ethyl undec-10-enoate	0.05
22	30.8	Ethyl-.beta.-(4-hydroxy-3-methoxy-phenyl)-propionate	0.04
23	31.3	Ethyl tetradecanoate	0.12
24	32.7	Tridecanoic acid, 12-methyl-, methyl ester	0.07
25	33.4	Ethyl palmitate	0.61
Alcohols			
26	3.5	3-methyl-1-butano	6.91
27	3.6	2-methyl-1-butano	4.75
28	4.7	2,3-Butanediol	8.35
29	5.9	1-Pentanol, 3-methyl-	0.05
30	9.6	n-Heptanol	0.03
31	9.9	1-Propanol, 3-(methylthio)-	0.78
32	12.8	1-Octanol	0.12
33	14.2	Phenethyl alcohol	22.18
34	28.1	Cedrol	0.04
Acids			
35	6.0	Butanoic acid, 3-methyl-	0.18
36	6.3	Butanoic acid, 2-methyl-	0.08
37	8.0	Butanoic acid, 4-hydroxy-	0.05
38	10.2	Hexanoic acid	0.68
39	16.3	Octanoic Acid	4.29
40	18.4	Pentanoic acid, 2-methyl-4-oxo-	0.13
41	19.0	Nonanoic acid	0.31
42	21.8	n-Decanoic acid	1.28
Phenols			
43	16.0	Phenol, 4-ethyl-	2.15
44	18.6	Phenol, 4-(2-propenyl)-	0.62
45	19.2	4-ethyl guaiacol	1.98
46	20.3	2-Methoxy-4-vinylphenol	5.66
47	21.5	Eugenol	0.64
48	24.0	(E)-Phenol, 2-methoxy-5-(1-propenyl)-	0.21
49	25.6	Phenol, 2,4-bis(1,1-dimethylethyl)-	0.89
Aldehydes			
50	13.8	Nonanal	0.05
51	21.6	(E)-2-Dodecenal	0.07
52	22.8	Dodecanal	0.09
53	24.6	2-Undecenal	0.07
54	31.6	n-Tetradecanal	0.03
55	12.7	Furaneol	0.32
Terpenes			
56	16.6	Terpineol	0.07
Others			
57	12.2	4-hexanolide	0.02

4 Conclusion

In this study, we investigated the volatile profile of pineapple peel wine by HS-SPME-GC/MS. Results obtained showed that there were abundant volatile components in the wine samples. A total of 57 volatiles were identified, including 25 esters, 9 alcohols, 8 acids, 7 phenolic compounds, 6 aldehydes and ketones, 1 terpene and 1 lactone, respectively. Among various aroma substances, the types of esters are the most, while the content of alcohols is the largest. Within these, phenethyl alcohol, 3-methyl-1-butano, 2-methyl-1-butano, 2,3-Butanediol and 2-Methoxy-4-vinylphenol were the major constituents. The work might help comprehensive insight into the flavor characteristics of pineapple peel wine and provide potential application of pineapple peel.

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