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Evaluation of volatile profiles obtained for minimally-processed pineapple fruit samples during storage by headspace-solid phase microextraction gas chromatography-mass spectrometry

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Abstract

This paper describes the application of the solid-phase microextraction (SPME) technique for the determination and monitoring of the volatile profile of minimally-processed pineapple fruit stored at various temperatures (-12 °C, 4 °C and 25 °C) for different periods (1, 4 and 10 days). The SPME fiber coating composed of Car/PDMS presented the best performance. The optimal extraction conditions obtained through a Doehlert design were 60 min at 35 °C. The profiles for the volatile compounds content of the fruit at each stage of storage were determined by gas chromatography-mass spectrometry (GC-MS). The variation in the volatile profile over time was greater when the fruit samples were stored at 25 °C and at -12 °C compared to 4 °C. Thus, according to the volatile profiles associated with the storage conditions evaluated in this study, packaged pineapple retains best its fresh fruit aroma when stored at 4 °C.

Keywords: volatile profile; pineapple; minimally processed; microextraction; gas chromatography.

Practical Application: The innovative ready-to-eat food products with fresh-fruit characteristics have gained prominence all over the world, since they are suitable for modern urban lifestyles, where the time available for food preparation is limited. Minimally-processed pineapple fruit represents an important product of consumers need. This work concludes the study to determine the best storage conditions of pineapple fruit from the aroma retention standpoint and thus recommends the fruit storage at 4 °C so as to retain best the quality of pineapple.

1 Introduction

Pineapple (*Ananas comosus*) is one of the most popular subtropical fruits cultivated and consumed worldwide. The fruits are consumed fresh and are also extensively used in the food industry for the production of canned fruit, jams/jellies and concentrated juice (Pino & Queris, 2010). A key issue regarding the marketing of tropical fruits is the search for efficient preservation methods in order to retain the inherent organoleptic quality of the product (Xisto et al., 2012).

Aroma is one of the most important attributes which affects the consumption of fruit from the tropics and subtropics. Since these fruits are often inexpensive and extremely rich in vitamins, their popularity has increased, especially in Europe and the United States. In Brazil, tropical fruits are mostly consumed *in natura*, but some of these are exported to other countries mainly in the form of frozen pulp (Bauer, 2000). In particular, the exotic aroma of pineapple fruit is widely appreciated by consumers (Steingass et al., 2015).

The determination of compounds which influence the aroma of any fruit is an important task, since these are related to the food quality. Different strategies for determining the volatile content of these matrices have been applied to isolate these compounds prior to their identification through chemical analysis. One very important technique in this regard is solid phase microextraction (SPME) (Arthur & Pawliszyn, 1990). SPME is an alternative solventless extraction procedure, which does not induce modifications in the volatile compounds due to temperature or solvent effects. This type of extraction involves the adsorption/absorption of analytes onto a fused silica fiber coated with a suitable stationary phase and their subsequent desorption immediately before chromatographic analysis (Kataoka et al., 2000; Merib et al., 2013). The use of SPME in the headspace mode (HS-SPME) has been successfully applied for the determination of the volatile profiles of several fruits such as passion fruit (Carasek & Pawliszyn, 2006), blueberry (Cheng et al., 2015), blackberry (D'Agostino et al., 2015), strawberry (Du et al., 2011), Black chokeberry (Kraujalyte et al., 2013), citrus fruits (Nardini et al., 2013; Rambla et al., 2014); grapes (Perestrelo et al., 2014) and study on pineapple harvest maturity (Steingass et al., 2014). In combination with this powerful sample preparation technique, an efficient separation/identification procedure is generally required. In order to achieve good performance in terms of the separation and identification of analytes for the determination of the volatile profiles of different matrices, gas

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chromatography coupled to mass spectrometry (GC-MS) has been used successfully.

Different methods for the preservation and storage of tropical fruits have been applied. The increasing demand for fresh, healthy, nutritious and ready-to-eat foods has stimulated the expansion of the minimally-processed fruits and vegetables (Barbosa et al., 2013). These innovative ready-to-eat (RTE) food products with fresh-fruit characteristics have gained prominence all over the world, since they are suitable for modern urban lifestyles, where the time available for food preparation is limited (Koidis et al., 2012). Minimally-processed fresh fruit represents an important component of a healthy diet and is a convenient way to increase the consumption of fresh produce (Siroli et al., 2014). In general, the operations of washing, sorting, peeling and cutting involved in the production of RTE products results in a reduction in the shelf life of the fresh-cut produce, when compared with the intact product (Conte et al., 2009).

Fresh fruit pieces stored in plastic packages are commonly found in supermarkets in Brazil and many tropical fruits are widely available in minimally-processed forms. These fruits are normally maintained under refrigeration for a certain period until their consumption. In this regard, the evaluation of the volatile profile of these fruit products during storage allows the best possible way to determine the retention of inherent fruit quality.

In this context, the objectives of this study were to optimize the conditions for the extraction of the volatiles fraction of minimally-processed pineapple fruit using the HS-SPME procedure and then to identify the volatile compounds under standardized analytical conditions by GC-MS. The volatile profiles of minimally-processed pineapple fruit stored for different time periods (1, 4 and 10 days) at refrigeration, room and freezing temperatures (4, 25 and -12 °C, respectively) were determined and based on the results obtained the best storage conditions for the retention of the aroma quality of the fruit were identified.

2 Experimental

2.1 Instrumentation

In the first part of this study, the optimization was performed on an Agilent Technologies gas chromatograph equipped with a flame ionization detector (Santa Clara, CA, USA) using a DB-5 chromatographic column (30 m × 0.25 mm × 0.25 μm). The oven temperature program was: 40 °C (held for 1 min) followed by heating at 5 °C min^{-1} to 240 °C. The injector and detector temperatures were 260 °C and 270 °C, respectively. Ultra-pure hydrogen at 1 mL min^{-1} was used as the carried gas. The injections were performed in splitless mode.

A Shimadzu gas chromatograph equipped with a mass spectrometry detector (Kyoto, Japan; GC-MS QP-2010 Plus) and a Restek Rtx®-5MS chromatographic column (30 m × 0.25 mm × 0.25 μm), obtained from Restek Corporation (Bellefonte, PA, USA), were used in this study for the determination of the volatile profiles and identification of the volatile compounds. The oven temperature program was: 40 °C (held for 1 min) followed by an increase of 5 °C min^{-1} to 240 °C. The injector temperature was 260 °C and the temperatures of the ion source and the interface were 270 °C and 260 °C, respectively. Ultra-pure helium was used as the carrier gas with a flow of 1 mL min^{-1}. The injection was performed in the splitless mode and the mass spectrometer was operated in electron impact (EI) ion source mode at 70 eV. In this analysis total ion chromatograms (TICs) were obtained. The SPME fiber desorption time was fixed at 25 min to avoid any carryover effect and the analysis of the volatile profile for each sample was performed in duplicate.

2.2 Reagents and materials

In this study, 40 mL vials (Supelco, Bellefonte, USA) with PTFE/silicon septa, a thermostatic bath (New Technique, São Paulo, Brazil) and an analytical balance (Mars Trade, Analytical Instrumentation, São Paulo, Brazil) were used.

To perform the microextractions, SPME fibers were used with the following polymeric coatings: PDMS/DVB (65 μm of thickness), PDMS (100 μm), DVB/Car/PDMS (50/30 μm), Car/PDMS (85 μm) obtained from Supelco (Bellefonte, Palo Alto, USA). A mixture containing alkanes (C_7 – C_{30}) at a concentration of 1000 μg mL^{-1} of each component in hexane (Sigma-Aldrich, Milwaukee, WI, USA) and sodium chloride P.A. (Vetec, Rio de Janeiro, Brazil) were also used in this study.

2.3 Sample preparation

Fresh pineapple was purchased from a supermarket located in the city of Florianópolis, Santa Catarina State, Brazil and transported to the Laboratory of Chromatography and Atomic Spectrometry at the Federal University of Santa Catarina. The fruit was washed with neutral detergent, then with NaOCl (200 mg L^{-1}) and finally with ultra-pure water. After 15 min the fruit was peeled and cut into small slices. These slices were placed on polystyrene plates, covered with PVC film, and then stored in a refrigerator (4 °C). For comparative studies, some of the samples were stored in a freezer (-12 °C) and others at room temperature (25 °C).

2.4 Optimization steps

Choice of fiber coating for HS-SPME procedure

In the first step of the optimization, the polymeric SPME fiber coating was selected. For this purpose, four different commercially-available polymeric coatings for SPME were tested: PDMS/DVB (65 μm of thickness), PDMS (100 μm), DVB/Car/PDMS (50/30 μm) and Car/PDMS (85 μm). In this step, 0.55 g of pineapple, previously prepared according to the procedure cited above, were placed in sealed vials with PTFE/silicon septa. These vials containing the fruit samples were maintained in a thermostatic bath programmed at 40 °C for 5 min to stabilize the temperature before the microextraction. After this short period, the polymeric coating was introduced into the sealed vials and the extractions were performed for 40 min. As previously mentioned, all optimization steps were performed in a gas chromatograph equipped with a flame ionization detector. The chromatographic analytical conditions are given above in the Instrumentation section. All of the analyses were performed in triplicate.

Evaluation of salting out effect

For the evaluation of the salting out effect, pineapple samples (0.55 g) were submitted to HS-SPME procedures in their raw form (with no addition of chemical reagents) and also with the addition of 5 mL of saturated NaCl solution. A SPME fiber composed of Car/PDMS (previously optimized) was used and the microextraction was performed applying an extraction time of 40 min at 40 °C. The chromatographic analysis conditions are given above in the Instrumentation section. All of the analyses were performed in duplicate.

2.5 Optimization of experimental conditions for the HS-SPME

The experimental conditions for the HS-SPME procedure were also optimized. A multivariate optimization according to a Doehlert design was carried out with triplicates at the central point and extraction times varying from 20 to 100 min (20, 40, 60, 80, 100) and extraction temperatures varying from 20 to 40 °C (20, 30, 40) were applied as the variables.

2.6 Determination of volatile profiles of pineapple samples

After the optimization steps, previously prepared pineapple samples (0.55 g) were subjected to the HS-SPME procedure using an SPME fiber composed of Car/PDMS, for the determination of the volatile profiles corresponding to different storage times and temperatures. The separation/detection of the compounds was performed by GC-MS and the identification was carried out using the National Institute of Standards and Technology (NIST) 05 library. In addition, the retention index for each compound was calculated and compared with data previously reported in the literature.

The packaged minimally-processed pineapple fruit samples were stored at 3 different temperatures: room temperature (25 °C), in a refrigerator (4 °C) and in a freezer (-12 °C). Pineapple samples were withdrawn after 1, 4 and 10 days to determine the volatile profile and all samples were analyzed in duplicate.

3 Results and discussion

3.1 Salting out effect

The effect of the addition of saturated NaCl solution on the efficiency of the extraction of the compounds from the pineapple fruit samples by HS-SPME was evaluated. Higher extraction efficiencies were obtained for the samples without the addition of saturated NaCl solution. Therefore, this condition was selected to perform the other optimization steps in this study.

3.2 SPME fiber coating optimization

The polymeric fiber coating was also optimized. In this procedure the sum of the chromatographic peak areas for all extracted compounds was considered as the response. The fibers composed of PDMS/Car/DVB and Car/PDMS presented higher extraction efficiency and the chromatographic peak areas obtained with these two fibers were very similar (Figure 1). However, the fiber composed of PDMS/Car/DVB revealed higher standard deviations when compared with Car/PDMS fiber. Therefore, the fiber composed of Car/PDMS was selected for the subsequent experiments. This bipolar polymeric coating presents good extraction capacity for several types of compounds due to the presence of carboxen (high extraction capacity for more volatile compounds) and also PDMS (high extraction efficiency for less volatile compounds). Moreover this fiber has been reported to be a better option for the determination of the volatile profile of several matrices which contain compounds with a wide range of volatility (Pawliszyn, 2009).

3.3 Optimization of extraction conditions

To determine the ideal conditions for the HS-SPME procedure, a multivariate optimization step was performed to determine the best extraction time and temperature. The sum of the chromatographic peak areas corresponding to all compounds was considered as the response and a Doehlert design was applied. In the Doehlert design, the variable extraction time was studied at five levels (20, 40, 60, 80 and 100 min) and the variable extraction temperature was evaluated at three levels (20, 30 and 40 °C). The response surface graph generated from these results is shown in Figure 2 while the experimental data related to ANOVA table are presented as Table 1.

As can be observed, higher responses were obtained applying an extraction time of 60 min at a temperature of 35 °C. Therefore, these extraction conditions were selected for the determination of the volatile profiles for pineapple fruit samples stored under different conditions.

3.4 Evaluation of volatile profiles obtained for pineapple samples

Pineapple samples stored at room temperature

In order to perform a detailed study, the chromatographic data were divided into 2 groups: the first group (more volatile compounds) was composed of compounds which eluted up to 12 min, while the second group (less volatile compounds) related to the

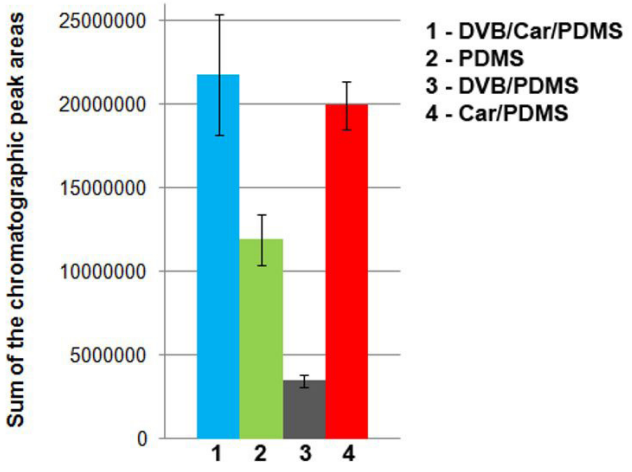

Figure 1. Effect of different polymeric fiber coatings on the total peak area on the chromatogram.

compounds which eluted after this time. The volatile profiles of the fruit samples stored at room temperature (25 °C) were determined considering three different storage periods (1, 4 and 10 days) and the data obtained are presented in the form of a bar graph (Figure 3) which shows the sum of the chromatographic peak areas related to the 'two groups' of volatile compounds.

From the bar graph shown in Figure 3 it can be clearly observed that there is a notable difference in the chromatographic peak areas corresponding to the volatile profile of the pineapple samples after different storage times, mainly related to more volatile compounds. For these compounds, there was a considerable increase in the chromatographic peak areas, mainly from the first to the fourth day of pineapple fruit storage. However, for the less volatile compounds the volatile profiles did not show major changes during storage. The chromatograms corresponding to each period of storage are provided in the Figure 4.

The main change in the chromatographic profile for the more volatile compounds (up to 12 min of elution) related to a large increase in the chromatographic peaks corresponding to the ethyl alcohol and ethyl acetate contents of the fruit samples after 4 days of storage as compared to the first day. These two compounds were also present on the first day of storage but with lower peak intensity and after the fourth day these compounds were predominant in the chromatograms. Moreover after the fourth day, the appearance of several methyl esters of carboxylic acids, such as 2-methylethyl propanoate, 2-methylethyl butanoate, 3-methylethyl butanoate and ethyl butanoate, was observed. Another important change was the appearance of ethanal, acetic acid, phenyl ethyl alcohol and 2-phenyethyl acetate and an increase in the chromatographic peak areas corresponding to 3-methyl-1-butanol and 2-methyl-1-butanol on the tenth day of storage at room temperature.

Other important variations in relation to the more volatile compounds were observed in the samples stored at room-temperature. There was a large decrease in the area of the chromatographic peak corresponding to methyl 3-(methylthio)propionate. This compound was not present in the chromatogram obtained for the fruit after the tenth day of storage. Sulfur compounds, for instance, methyl 3-methylthiopropionate, have been previously found in a wide variety of food substances. In several cases, these compounds are major contributors to the odor and flavor of foods (Kaewtathip & Charoenrein, 2012). Another important factor to be taken into account is a sharp decrease in the intensity of the chromatographic peak corresponding to methyl hexanoate,

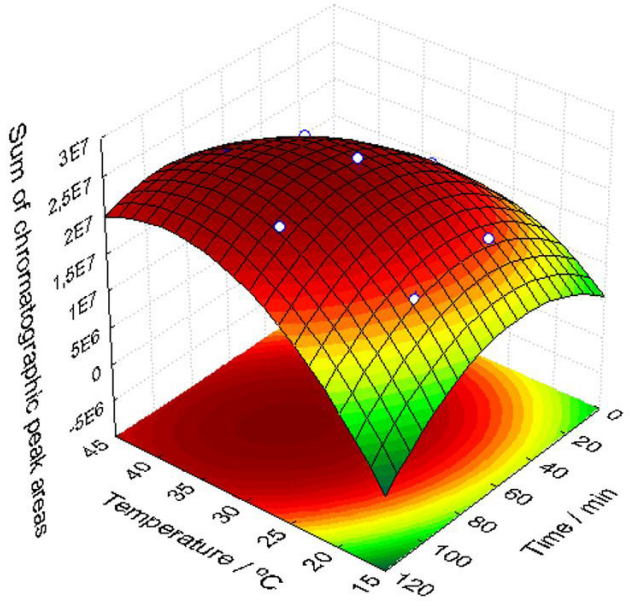

Figure 2. Response surface obtained from a Doehlert design for the variables of extraction time and extraction temperature.

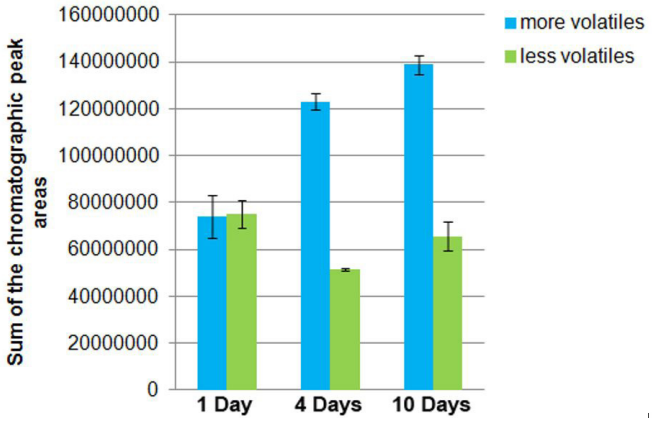

Figure 3. Bar graph representing the sum of the chromatographic peak areas for compounds extracted from pineapple fruit samples stored at room temperature (25 °C).

Table 1. ANOVA processing data related to Doehlert design.

Factor	SS	df	MS	F	p
Temperature, °C (L)	3.503977E+13	1	3.503977E+13	21.09195	0.044286
Temperature, °C (Q)	2.996156E+13	1	2.996156E+13	18.03515	0.051224
Time, min (L)	9.546719E+12	1	9.546719E+12	5.74658	0.138709
Time, min (Q)	1.240572E+13	1	1.240572E+13	7.46754	0.111883
1L by 2L	5.864631E+12	1	5.864631E+12	3.53017	0.201033
Error	3.322573E+12	2	1.661287E+12		
Total SS	8.697734E+13	7			

R^2 = 0.9618; Adj: 0.8663; 2 factors, 1 Block, 8 Runs; MS Residual=166129E7.

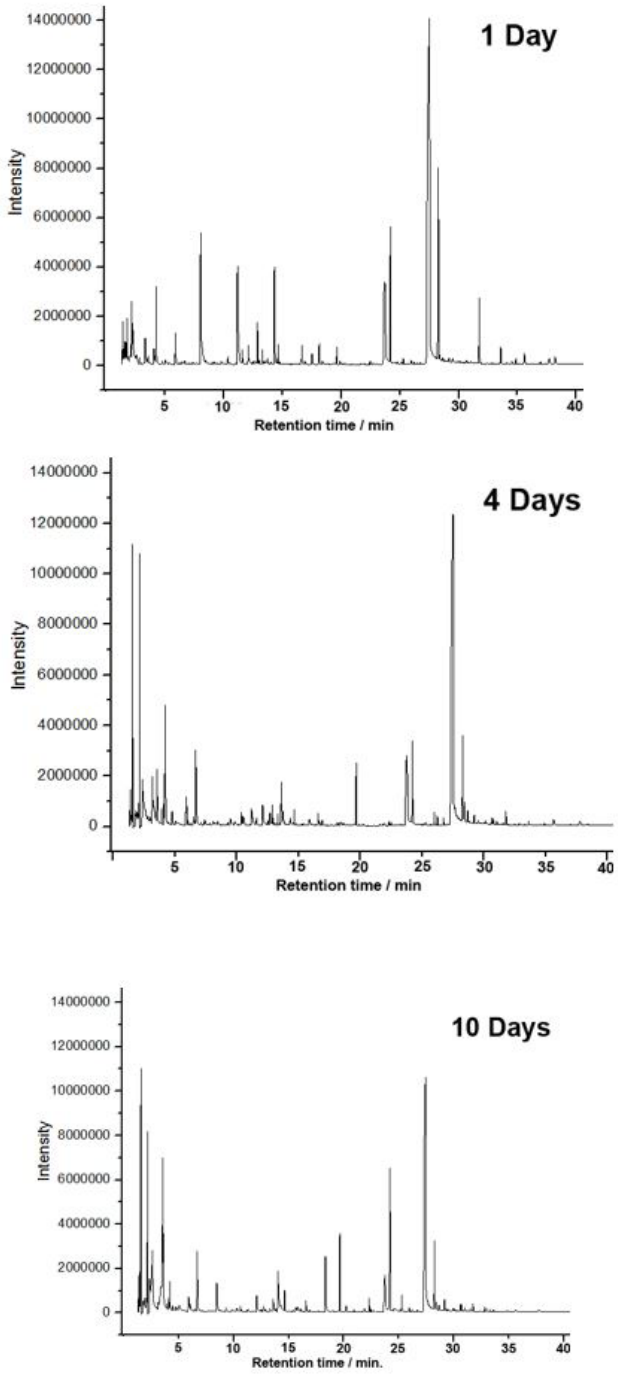

Figure 4. Chromatograms obtained from pineapple samples stored at room temperature (25 °C)

which is known to be an important compound in relation to the characteristic aroma of the pineapple fruit.

Regarding the less volatile compounds extracted from the samples stored at room temperature, some changes in the volatile profiles were observed. In this case, the sum of the peak areas varied to a lesser degree compared to the more volatile compounds, which can be observed from the bar graph shown in Figure 5. The main changes observed for this group are related to a decrease in the peak intensity for γ-hexalactone. This compound, along

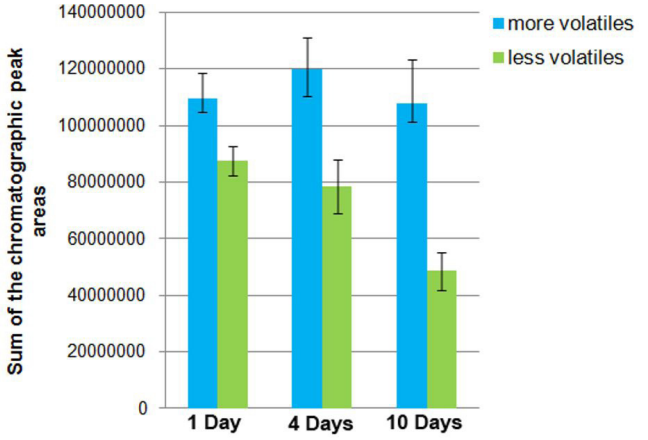

Figure 5. Bar graph representing the sum of the chromatographic peak areas of compounds extracted from pineapple fruit samples stored in a refrigerator (4 °C).

with 5-alkylpentanolides (δ-lactones) and 4-alkylbutanolides (γ-lactones), is an important contributor to the typical flavor of a broad range of fruits and fruit products (Steingass et al., 2015). Other compounds, such as methyl 2-methyl butanoate, methyl 4-oxopentanoate and decanal, also showed a decrease in the peak intensity. For some less volatile compounds, for instance, 2-phenylethyl acetate, an increase in the size of the chromatographic peak areas was observed.

Pineapple samples stored in refrigerator

The volatile profiles of minimally-processed pineapple samples stored at 4 °C were also obtained. The extraction and analysis procedures were the same as those employed for fruit samples stored at room temperature (25 °C). SPME analysis was performed at three different storage times (1, 4 and 10 days) and the sum of the chromatographic peak areas of each chromatogram was used to verify the changes in the volatile profile over time.

The bar graph in Figure 5 shows the changes in the sum of the chromatographic peak areas for the more volatile (elution time of up to 12 min) and for less volatile (elution time greater than 12 min) compounds.

According to the bar graph (Figure 5), it was observed that the main differences were related to the less volatile compounds and this occurred mostly in the case of fruit stored for 10 days. On comparing the volatile profiles obtained for the samples after one and four days of storage, and taking into account the error bars associated with each analysis, very small changes occurred in the samples stored at 4 °C for both types (less volatile and more volatile) of compounds. This was not the case for the samples stored at 25 °C (shown in Figure 3), where there was a considerable difference in the chromatograms obtained for fruits stored for one and four days. The chromatograms corresponding to each period of storage are provided in Figure 6.

This finding represents a very useful indicator that the fresh aspect of pineapple can be maintained for a longer time if the

fruit pieces are maintained refrigerated in comparison to their storage at room temperature.

The main changes in the chromatographic profiles for the samples stored at 4 °C, which were related to the less volatile compounds (elution time of up to 12 min), were an increase in the chromatographic responses for ethyl acetate and methyl acetate. However, the changes in the volatile profiles were less intense when compared to those observed for the fruit samples stored at room temperature.

The chromatographic responses for two important aroma compounds (methyl 3-methylthiopropionate and methyl hexanoate) in the pineapple fruit were less affected when minimally-processed pineapple fruit was stored at 4 °C. Based on the chromatograms obtained for the fourth and tenth day of fruit storage at room temperature, these compounds were practically not detected in both cases. However, for samples stored at 4 °C these compounds were detected even in fruit stored for 10 days, indicating a better retention of the aroma characteristics of the fresh fruit.

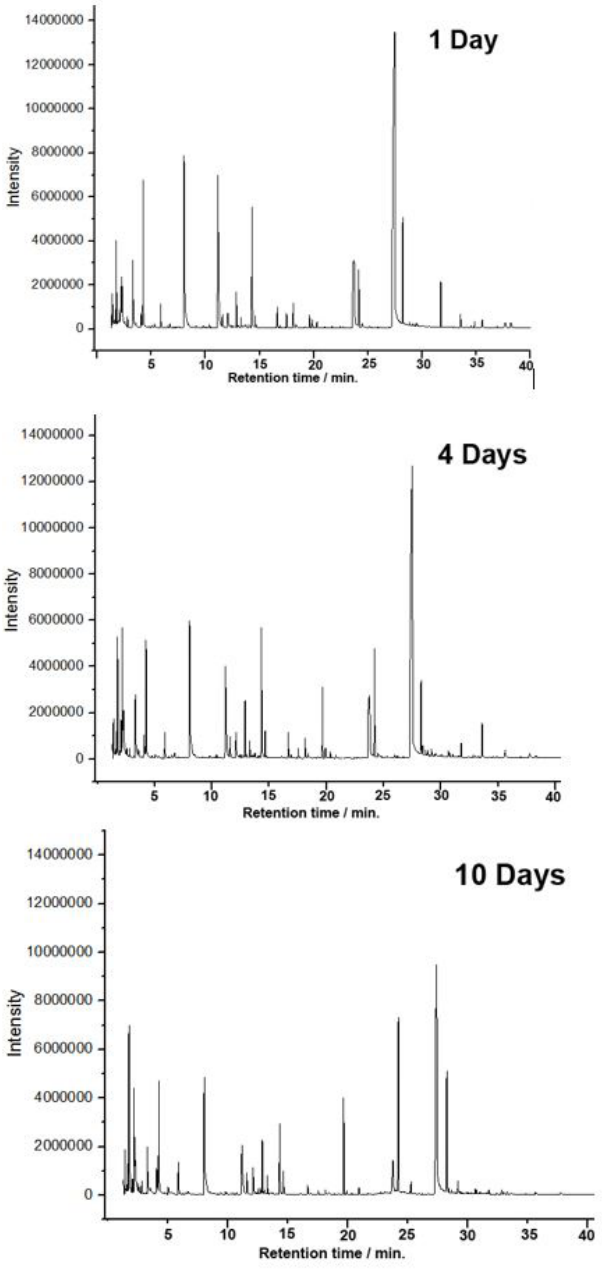

Figure 6. Chromatograms obtained from pineapple samples stored refrigerated (4 °C).

Another important factor associated with the storage of fruit at 4 °C was the presence of a much reduced chromatographic response related to ethanol when compared to samples stored at room temperature, probably due to a decrease in the rate of the conversion of some carbohydrates into ethanol by alcoholic fermentation.

For the less volatile compounds, low-temperature storage also presented excellent results, as these fruits maintained the original chromatographic profile of the pineapple samples. For the SPME performed on the first and fourth days of fruit storage very small differences were observed in the chromatographic peaks, which indicate that the aroma of the fruit was preserved in these samples. Also, for the fruit subjected to ten days of storage, the chromatographic peaks corresponding to important aroma impact compounds of pineapple viz., 3-hydroxyhexanoate, ethyl 2,2-dimethylpentanoate, methyl 7-oxooctanoate and methyl decanoate showed very small decreases in their chromatographic responses.

Changes in the volatile profile of frozen pineapple samples

The chromatographic profiles for the samples stored in the freezer at a temperature of approximately -12 °C were also obtained. The extraction procedure and chromatographic analysis of the pineapple fruit samples stored at -12 °C were the same as those applied to the fruits stored at room temperature or at 4 °C. Figure 7 shows the bar graph representing the sum of the chromatographic peak areas for both types of compounds obtained for fruit stored at -12 °C for different periods of time.

As can be seen in Figure 7, a reduction in the values corresponding to the sum of the chromatographic peak areas

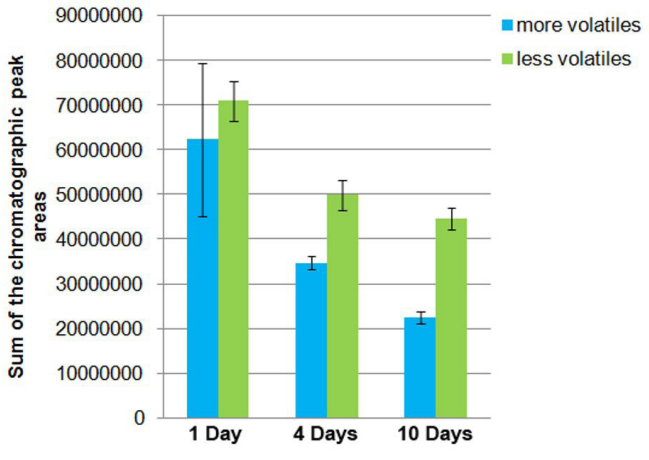

Figure 7. Bar graph representing the sum of the chromatographic peak areas of compounds extracted from pineapple samples stored in a freezer (-12 °C).

was observed with an increase in the storage period, particularly from the first to the fourth days of storage, for both classes of compounds. This decrease provides evidence that the volatile profile for the frozen fruit sample was not the same as that obtained for the fresh fruit. The chromatograms corresponding to each period of storage are provided in Figure 8.

For the group of more volatile compounds, there was a sharp decrease in the chromatographic peak areas for some compounds, for instance, methyl acetate, ethyl acetate, methyl 2-methyl butanoate, methyl hexanoate and methyl 3-(methylthio) propionate. Moreover in relation to the group of less volatile compounds, a large decrease was observed for methyl octanoate, ethyl octanoate and methyl decanoate.

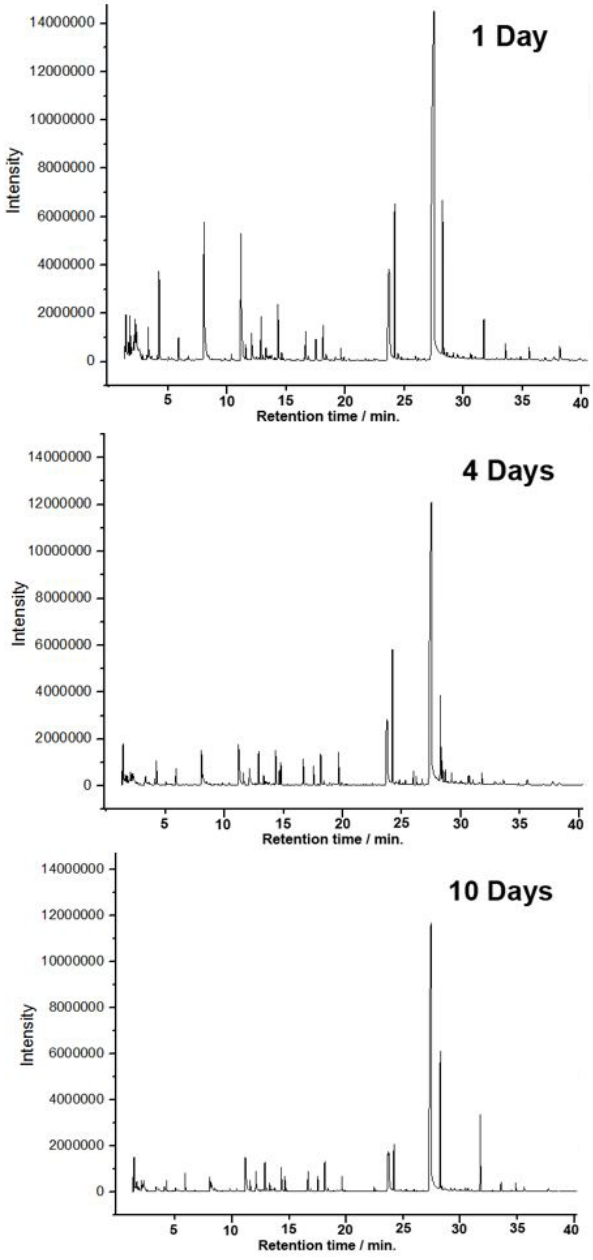

Figure 8. Chromatograms obtained from pineapple samples stored frozen (-10 °C).

Kaewtathip and Charoenrein (Kaewtathip & Charoenrein, 2012) studied the changes in the volatile profiles obtained for pineapple samples of the Smooth Cayenne variety during freezing and thawing. These researchers also observed a decrease in the chromatographic responses, mainly for esters, which are important constituents of the fresh characteristic aroma of pineapple. This decrease could have occurred due to the fruit cells being damaged during freezing and degradation of the cell structure when the pineapple is thawed, which could lead to a loss in aroma following the oxidation of the aroma compounds. Freeze–thaw cycles applied to pineapple can reduce the quantity of many of the important aroma compounds and thus the overall flavor quality.

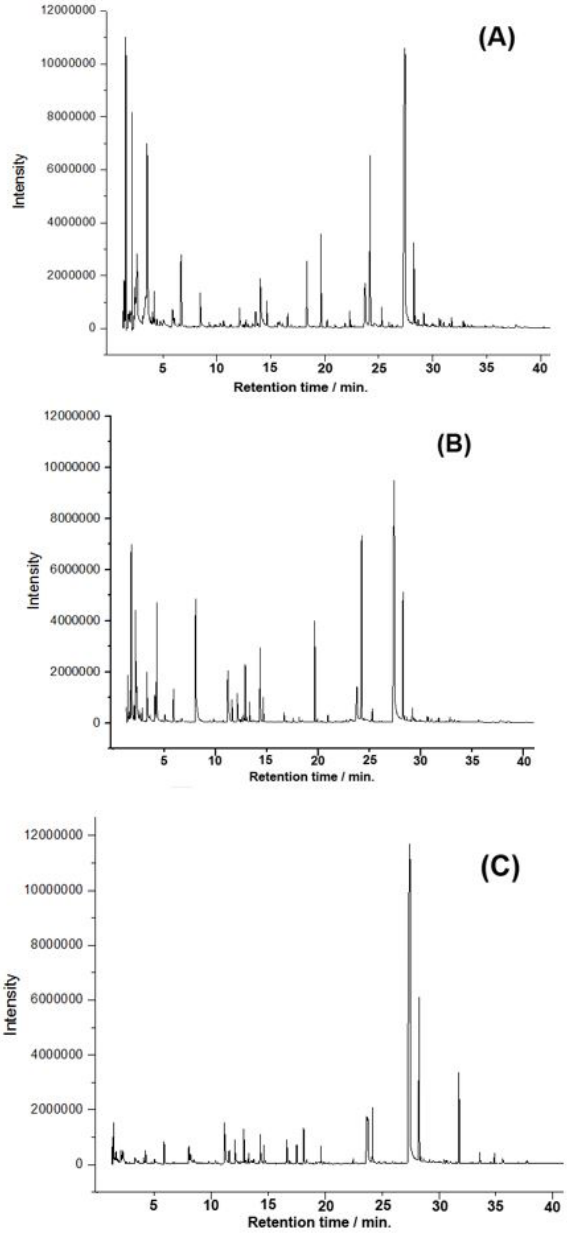

Figure 9. Chromatograms obtained for the minimally-processed pineapple fruit on the tenth day of storage at 25 °C (A); 4 °C (B); and at -12 °C (C).

3.5 Identification of the compounds extracted by HS-SPME

After the volatile profile for each storage period had been obtained, a table showing the tentative identification of all compounds was compiled (Table 2). Also, in this table the retention indices obtained for these compounds are compared with the values reported in the literature.

In addition, the chromatograms corresponding to the tenth day of storage of the pineapple samples can be observed in Figure 9 as follows: Figure 9A stored at room temperature (25 °C); Figure 9B stored at 4 °C; and Figure 9C stored at -12 °C.

According to these chromatograms, after a storage period of 10 days, a considerable difference between the samples stored at -12 °C and those stored at the other temperatures can be observed. In this case, the chromatographic peaks presented much lower intensity, which strongly indicates a change in the characteristics of the samples after storage in a freezer.

Table 2. Volatile compounds extracted by SPME from minimally-processed pineapple fruit stored at different temperatures and time periods.

Compounds*	RI_{Calc*}	RI_{Liter}	25° C			4° C			-12 °C		
			1	4	10	1	4	10	1	4	10
Esters											
methyl acetate	557	-	x	x	x	x	x	x	x	x	x
ethyl acetate	617	614	x	x	x	x	x	x	x	x	x
methylpropanoate	632	621	x	x	x	x	x	x	x	x	x
methylisobutyrate	685	-	-	-	-	x	x	x	-	-	-
methyl 2-methylpropanoate	686	684	x	x	x	x	x	x	x	x	x
ethylpropanoate	711	714	x	x	x	x	x	x	x	x	x
n-propylacetate	713	714	-	-	-	-	-	-	x	x	x
methylbutanoate	720	724	x	x	x	x	x	x	x	x	x
2-methyl ethylpropanoate	755	755	-	x	x	-	-	-	-	-	-
2-methylpropyl acetate	771	-	x	x	x	x	x	x	x	x	x
2-methyl methylbutanoate	774	-	x	x	x	x	x	x	x	x	x
methylpentanoate	823	820	x	-	-	x	x	x	x	x	
methyl 2-hydroxy-2-methylbutanoate	845	-	x	x	x	x	x	x	x	x	x
ethyl 2-methylbutanoate	846	842	-	x	x	-	-	-	-	-	-
ethyl 3-methylbutanoate	852	847	-	x	-	-	-	-	-	-	-
2-methyl butyl acetate	875	876	x	x	x	x	x	x	x	x	x
3-methyl butyl acetate	878	876	x	x	x	x	x	x	-	-	x
methylhexanoate	924	924	x	x	-	x	x	x	x	x	x
ethyl 3-hydroxybutanoate	937	-	x	x	x	x	x	x	x	x	x
2-hydroxy 3-methyl ethylbutanoate	965	-	-	x	x	-	-	-	-	-	-
ethylhexanoate	999	996	x	x	x	x	-	-	x	x	x
ethyl 3-hexenoate	1007	-	x	x	x	x	x	x	x	x	x
methyl 3-(methylthio)propanoate	1024	1027	x	x	x	x	x	x	x	x	x
methylacetoacetate	1038	-	x	x	-	x	x	x	x	x	x
2,3-butanedioldiacetate	1066	-	x	x	x	x	x	x	x	x	x
methyl 2-methyl 3-oxobutanoate	1078	-	x	x	-	x	x	x	x	x	x
methyl 4-oxo-pentanoate	1091	-	x	x	x	x	x	x	x	x	x
methyl 4-(methylthio)butanoate	1101	-	x	x	x	x	x	x	x	x	x
methyloctanoate	1123	1126	x	x	-	x	x	x	-	-	-
ethyl 3-hydroxyhexanoate	1168	-	x	x	x	x	x	x	x	x	x
ethyloctanoate	1197	1196	x	x	x	x	-	-	x	x	x
methyl 3-hydroxyhexanoate	1199	1049	x	x	x	x	x	x	x	x	x
ethyl 2,2-dimethylpentanoate	1227	-	x	x	x	x	x	x	x	x	x
methyl 7-oxooctanoate	1249	-	x	x	x	x	x	x	x	x	x
phenyl ethyloctanoate	1254	-	-	-	-	x	x	x	-	-	-
2-phenyl ethyl acetate	1255	1256	-	-	-	x	x	x	-	-	-
methyldecanoate	1323	1325	x	-	-	x	x	-	x	-	-
ethyl 4-(*E*)-decenoate	1379	-	x	x	x	x	x	x	x	x	x
ethyldecanoate	1393	1397		x	x	x	x	x	-	-	-

x- co Compound detected; - com Compound not detected. * tenTentatively identified by mass spectrometry and from the retention index (calculated and obtained from the literature (Adams, 1995; Kondjoyan & Berdagué, 1996; Pino et al., 2005)).

Table 2. Continued...

Compounds*	RI_{Calc*}	RI_{Liter}	25° C			4° C			-12 °C		
			1	4	10	1	4	10	1	4	10
Alcohols											
ethanol	528	-	x	x	x	x	x	x	x	x	x
3-ethoxy-1-propanol	844	-	-	x	x	-	-	-	-	-	-
1-hexanol	869	867	-	x	-	-	-	-	-	-	-
1-heptanol	971	969	-	x	-	-	-	-	-	-	-
1-octanol	1072	1070	x	x	x	x	x	x	x	x	x
1-hepten-3-ol	1083	-	-	x	-	-	-	-	-	-	-
1-nonanol	1173	-	-	-	-	x	-	-	-	-	-
2-methyl 1butanol	732	734	x	-	x	x	x	x	x	x	x
3-methyl 1butanol	736	734	x	x	x	-	-	-	-	-	-
3-methyl-1-hepten-3-ol	1083	-	x	x	-	x	x	x	x	x	x
phenyl ethyl alcohol	1103	1122	-	x	x	-	-	-	x	x	x
Aldehydes											
ethanal	515	528	-	x	x	-	-	-	-	-	-
2-methylpentanal	543	-	x	-	x	x	x	x	x	x	x
3-hydroxybutanal	577	-	x	x	x	x	x	x	x	x	x
octanal	1003	1004	x	x	x	x	x	x	x	x	x
nonanal	1105	1106	x	x	x	x	x	x	x	x	x
decanal	1206	1207	x	x	x	x	x	x	x	x	x
Lactones											
5-ethyldihydro-2(3h)-furanone (γ hexalactone)	1053	1065	x	x	x	x	x	x	x	x	x
5-buthyldihydro-2(3h)-furanone (γ octalactone)	1256	-	x	x	x	x	x	x	x	x	x
6-butyltetrahydro-2h-pyran-2-one (δ nonalactone)	1282	1270	x	-	-	x	x	-	x	x	x
Others											
diethyl carbonate	785	776	x	x	x	x	x	x	x	x	x
acetic acid	664	-	x	x	x	x	x	x	x	x	x

x- co Compound detected; - com Compound not detected. * tenTentatively identified by mass spectrometry and from the retention index (calculated and obtained from the literature (Adams, 1995; Kondjoyan & Berdagué, 1996; Pino et al., 2005)).

4 Conclusions

The application of SPME to evaluate the volatile profile of fruit samples has been an important tool to verify the quality of the aroma of the minimally processed fruits. In this study, it was possible to verify that the pineapple samples stored at 4 °C and in the fourth day of storage presented similar chromatographic profile if compared to samples analyzed in the first day of storage. With these results it can be concluded that the aroma of the fresh fruit was preserved during this time of storage along with the inherent characteristics of the fresh fruit. For the samples stored at -12 °C and at 25 °C, the analyses of the chromatographic profile showed large differences between the first and the fourth day of storage, which reveals that the characteristics of the fresh fruit varied during the storage in these both forms. This occurrence is not interesting to minimally processed fruits stored at supermarkets due to the possibility of loss of quality of the fresh fruits before the consumption of the product.

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