Influence of fruit logistics on fresh-cut pineapple (*Ananas comosus* [L.] Merr.) volatiles assessed by HS-SPME–GC–MS analysis

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Abstract

Green-ripe pineapples are shipped overseas by sea freight, while those picked at full maturity need to be transported by airfreight over the same large distance. In this study, fresh-cut pineapple cubes were assessed two, five, and eight days after processing from green-ripe pineapples after mimicked sea freight (SF) and fully ripe air-freighted (AF) pineapples. The sea-freighted samples displayed elevated titratable acidity (TA), thus resulting in smaller ratios of total soluble solids and TA compared to the AF pineapples. Differences in the carotenoid levels of the two fresh-cut categories were found to be insignificant. By contrast, hierarchical cluster analysis (HCA) and principal component analysis (PCA) calculated on the basis of the volatiles analysed by headspace solid-phase microextraction–gas chromatography–mass spectrometry (HS-SPME–GC–MS) permitted to distinguish all six individual sample types and to segregate them into two major clusters (SF and AF). The effect of storage on the volatiles was further evaluated by partial least squares (PLS) regression. Substantial chemical markers to differentiate the individual samples and to describe the effect of storage were deduced from the PCA and PLS regression, respectively. In general, fresh-cut products obtained from fully ripe AF fruit displayed higher concentrations of volatiles, in particular, increased concentrations of diverse methyl esters. With progressing storage duration, the concentrations of ethanol and diverse ethyl esters increased. Moreover, products from AF pineapples displayed lower microbial counts compared to those from SF fruit.

Keywords Volatiles · Profiling analysis · Supply chain · Fruit logistics

Abbreviations

AF	Fully ripe air-freighted pineapple	HCA	Hierarchical cluster analysis
dap	Days after processing	HS-SPME–GC–MS	Headspace solid-phase microextraction–gas chromatography–mass spectrometry
d_f	Film thickness		
FW	Fresh weight	LRI	Linear retention index
GSP	Glutamate starch phenol red (agar)	LV	Latent variable
		PCA	Principal component analysis
		PC	Principal component
		PLS	Partial least squares
		RAE	Retinol activity equivalent
		SF	Green-ripe sea-freighted pineapple
		TA	Titratable acidity
		TPC	Total plate count
		TSS	Total soluble solids
		VID	Variable identification (coefficient)
		VRBD	Violet red bile dextrose (agar)

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Introduction

Owing to their exotic flavour, consumers in Europe and North America highly appreciate tropical fruits and products derived thereof. In the pineapple market, fresh fruit and fresh-cut products represent still growing sectors. Two principal logistic chains have been established for supplying the European market with fresh-cut pineapples. The first is based on harvesting fully ripe fruit, which are processed in close proximity to their production sites and then immediately exported by rapid airfreight [1]. For instance, the German and Britain markets are majorly supplied with this premium niche product by two major companies air-freighting fresh-cut fruits from Ghana to Europe [2]. The second chain is based on harvesting early green-ripe pineapples having an extended shelf life under chilled conditions, which permits their transport for multiple weeks by cargo ships. The major proportion of these sea-freighted pineapples is sold on the fresh fruit market. With regard to fresh-cut product manufacture, processing facilities located, e.g., in Europe and North America mostly rely on such sea-freighted fruit.

Pineapple volatiles have been intensely studied during the past decades [3]. In a previous study, fully ripe air-freighted pineapples and three post-harvest stages of green-ripe, sea-freighted fruit were assessed by solid-phase microextraction and gas chromatography–mass spectrometry (HS-SPME–GC–MS), revealing clear-cut differences in their volatiles [4]. In addition, the odour, taste, and overall preference of air-freighted pineapples were significantly better rated by a consumer panel compared to sea-freighted fruit assessed at two post-harvest stages [5]. By analogy to fresh fruit, also quality of fresh-cut products obtained from fully ripe and green-ripe sea-freighted pineapples may differ.

The volatiles of fresh-cut pineapples were investigated by Spanier et al. [6] during a 10-day storage period. Lamikanra [7] reported the involvement of esterases in the development of staleness in sliced pineapples. The effects of ultraviolet (UV) light irradiation [8] and modified atmosphere packaging [9] on fresh-cut pineapple volatiles were assessed. Using an electronic nose, Torri et al. [10] successfully described changes in aroma profiles of cut pineapple flesh stored at different temperatures. However, the influence of harvest maturity and fruit logistics on the composition of volatiles of fresh-cut pineapples has been disregarded in the aforementioned reports.

In the present study, volatiles of fresh-cut pineapple obtained from fully ripe fruit (“air freight”) and pineapples harvested at an earlier green-ripe stage that were stored for 14 days prior to processing (“sea freight”) were monitored by HS-SPME–GC–MS and multivariate statistical

data analysis. In addition, drip loss, pH, total soluble solids (TSS), titratable acidity (TA), carotenoid levels, and microbial quality of the two fresh-cut categories were assessed.

Materials and methods

Fresh-cut samples

Green-ripe and fully ripe pineapples (*Ananas comosus* [L.] Merr. cv. ‘MD2’ (syn. “Extra Sweet”)) were obtained from Jei River Farms (Opeman, Ghana). Green-ripe fruits were harvested ~137–145 days after ethylene induced flower induction (synchronisation) at a TSS of ~9.5–10 °Brix. According to Ghanaian post-harvest procedures for local market and airfreight export, fruits allowed to ripen on-plant were harvested ~147–157 days after synchronisation (~11 °Brix), i.e., 10–12 days later than those destined for dispatch by sea freight. For “de-greening”, green-ripe and fully ripe pineapples were treated with approx. 20 and 10 ppm ethylene, respectively, five days prior to harvest. Pineapples of both categories were harvested by hand and brought to the farm (15 km distance from the field) using a pick-up truck. Subsequently, the pineapples were dispatched to the processing facility (ca. 50 km) using a truck. Prior to processing, green-ripe pineapples were stored at 8 °C for 14 days, mimicking their sea freight export from West Africa or Central America to Europe. The fully ripe pineapples were processed within 24 h after harvest.

Flesh cylinders of 83 × 95 mm were obtained with a commercial processing machine. Cores were stamped out using a 26-mm bore hollow knife. The fruit flesh was sliced into rings of 1 cm thickness that were cut into eights. Bits obtained were subsequently dipped into aqueous citric acid solution (20 g/L) and allowed to drip off. Portions of 400 ± 5 g were packed into lockable plastic containers (185 × 145 × 55 mm, Safe-t-fresh, Inline Plastics, Shelton, CT, USA). Following packaging, the fresh-cut samples from green-ripe fruit processed after 14 days of storage at 8 °C and those from fully ripe pineapples were transported to Accra airport and air-freighted to Frankfurt (Germany) lasting approx. 6–7 h. Upon arrival, the samples were dispatched by a forwarding agent to their final destination in Stuttgart. Storage temperature during dispatch and subsequent storage was 8 °C.

Fresh-cut samples were analysed two, five, and eight days after processing (dap). Thus, the relevant shelf life period from the first day of the products’ availability on the European market (2 dap) to the end of the commercial shelf life (8 dap) was considered. Two packages of each fresh-cut category and storage stage were analysed in analytical duplicates ($n = 4$).

Reagents

Sodium chloride was pre-conditioned at 105 °C for minimum 24 h prior to use. 2-Methyl-1-pentanol, (all-*E*)- β -carotene, (all-*E*)-violaxanthin, sodium hydroxide, and potassium hydrogen phthalate were purchased from Sigma Aldrich (Taufkirchen, Germany). Purified water was prepared with an ultrapure water system type arium® 611 UV (Sartorius, Göttingen, Germany) and subsequently boiled for at least 20 min.

Physicochemical characterisation

The drip loss, i.e., the liquid drained from the pineapple chunks was determined gravimetrically. The pH and TSS were assessed with an InoLab 720 pH-meter (WTW, Weilheim, Germany) and a Rx-5000 Abbe refractometer (Atago, Tokyo, Japan), respectively. TA expressed as g citric acid per 100 g of fresh weight (FW) was determined with a Titrino 702 SM (Metrohm, Herisau, Switzerland) titration system [4]. The concentrations of (all-*E*)- β -carotene and total carotenoids were determined by HPLC–DAD as detailed elsewhere [11]. Retinol activity equivalents (RAEs) were calculated by converting 12 μ g dietary (all-*E*)- β -carotene to 1 μ g RAE [12].

Analyses of volatiles

Volatiles were analysed applying an Agilent GC–MS system type 6890 N coupled to an Agilent 5975 Mass Selective Detector (both Agilent Technologies, Santa Clara, CA, USA) as reported previously [4]. Briefly, 110 g pineapple flesh, 10 mL purified water, and 30 g sodium chloride were spiked with the internal standard 2-methyl-1-pentanol and homogenised using a laboratory blender. An aliquot of 8.0 ± 0.1 g of the puree obtained was filled into a 20-mL headspace vial. Volatiles were isolated from the headspace of the sample tempered to 30 °C using a polydimethylsiloxane/divinylbenzene fibre (65 μ m PDMS/DVB, StableFlex®, Supelco 57293-U, Sigma Aldrich) during an incubation time of 60 min.

Volatiles were desorbed for 1 min in the splitless mode at a temperature of 250 °C. Carrier gas was helium at a constant flow rate of 1.2 mL/min. GC separation was achieved using a fused silica capillary column coated with a polar polyethylene glycol (PEG) stationary phase (30 m $\times$ 0.25 mm, d_f = 0.25 μ m DB-Wax, Agilent J&W Columns, Santa Clara, CA, USA). The temperature program applied was as follows: isothermal hold at 60 °C (1 min), constant raise to 170 °C (3 °C/min) followed by a ramp to 220 °C (10 °C/min) with a final hold time of 10 min. Total run time was 53 min [4]. For validation of peak identity, the system described above was equipped with a fused silica column coated with a slightly

polar 5% phenyl-containing polydimethylsiloxane stationary phase (30 m $\times$ 0.25 mm, d_f = 0.25 μ m HP-5ms, Agilent J&W Columns). The following temperature program was applied: isothermal hold at 40 °C (1 min), constant raise to 180 °C (5 °C/min) followed by a ramp to 250 °C (10 °C/min) with a final hold time of 5 min. Total run time was 41 min [4].

Individual compounds were identified on the basis of their mass spectra compared to Wiley 6N library (Wiley and Sons, NY, USA) and literature data [13, 14]. Linear retention indices (LRI) according to Van den Dool and Kratz [15] were calculated relative to *n*-alkanes. Concentrations of the individual volatiles in μ g/100 g were expressed as equivalents of the internal standard 2-methyl-1-pentanol.

Microbiological analyses

A representative sample of 25 g of fresh-cut pineapple was taken from a sealed package and blended with 225 mL of sterile physiological NaCl solution in a sterile stomacher bag with lateral filter for 120 s using a Stomacher 400 Circulator (Seward, London, UK). Decimal dilutions of each homogenized sample were prepared in the same diluent and surface spread plated in duplicate on the respective agars. Total aerobic mesophilic plate counts (TPCs) and *Pseudomonas* spp. viable counts were determined on standard I nutrient (VWR, Darmstadt, Germany) and glutamate starch phenol red (GSP) agar (Merck, Darmstadt, Germany), respectively. *Enterobacteriaceae* viable counts were assessed using violet red bile dextrose (VRBD) agar (Oxoid, Basingstoke, UK) as previously reported [16]. Yeast and mould plate counts were determined using yeast extract glucose chloramphenicol (YGC) agar (Oxoid). Plates were incubated aerobically at 30 °C for 48 h on standard I and GSP agar. Prior to evaluation, samples surface spread on VRBD and YGS agar were incubated at 37 °C for 24 and 72 h, respectively. Microbial loads were expressed as colony-forming units (CFU) in log scale per gram ($\log_{10}$ CFU/g).

Statistics

Data obtained by HS-SPME–GC–MS were evaluated by PCA, HCA, and PLS regression calculated using Solo software (release 7.3.1, Eigenvector Research, Wenatchee, WA, USA). The PLS regression biplot was drawn with OriginPro 8 (OriginLab, Northampton, MA, USA) as detailed elsewhere [4, 17].

Compounds relevant for class separation in the PCA were calculated by summarising the absolute value of the loadings multiplied with the variance explained by the corresponding principal component [18]. The most discriminative volatiles describing the effect of storage were deduced from the PLS regression using variable identification (VID) coefficients [17, 18].

Significant ($p < 0.05$) differences of means of the physicochemical traits and the microbial loads were determined by analysis of variance (ANOVA) and Tukey's test, applying SAS version 9.4 (SAS Institute, Cary, NC, USA).

Results and discussion

Physicochemical characterisation

Physicochemical traits of fresh-cut products from fully ripe air-freighted and green-ripe pineapples after mimicked sea freight are compiled in Table 1. Irrespective of their logistic history, drip loss increased from 5.2–5.4 to 7.2–7.4% with progressing storage duration of all fresh-cut samples. Both fresh-cut categories displayed comparable TSS of 10.50–10.90 and 10.83–11.10 °Brix as determined in the products made from fully and green-ripe pineapples, respectively. By contrast, significantly elevated titratable acids amounting to 0.50–0.53 g/100 g of FW were determined in the samples from green-ripe fruit (fully ripe: 0.36–0.40 g/100 g of FW). Correspondingly, the TSS/TA, approximating the sugar-to-acid ratios of the fully ripe pineapples ranging between 27.5 and 29.9 g/g exceeded those of the sea-freighted samples of merely reaching levels between 21.2 and 22.1 g/g.

The concentrations of (all-*E*)-β-carotene among all samples amounted to values between 30 and 38 µg/100 g of FW. This provitamin A precursor contributed up to 6–10% of the total carotenoids that ranged between 374 and 518 µg/100 g of FW. The total carotenoids tended to decline at the end of the storage experiment (8 dap), although not reaching statistical significance ($p < 0.05$). The retinol activity equivalents (RAEs) amounted to 2.5–3.2 µg RAE/100 g of FW, thus being in the range of the 0.3 to 7.3 µg RAE/100 g of FW previously reported in the flesh of 'Sugar Loaf', 'Smooth

Cayenne', 'MD2', and 'Queen Victoria' pineapples from Ghana [11]. In the present study, the impact of harvest maturity and post-processing storage on the (all-*E*)-β-carotene and total carotenoid levels of fresh-cut pineapples were found to be insignificant and thus, not further investigated.

HS-SPME–GC–MS profiling analysis

Assignment of fresh-cut pineapple volatiles

Table 2 compiles the HS-SPME–GC–MS data of fresh-cut pineapple volatiles. A total of 131 peaks was detected. Among the tentatively assigned compounds, 91 esters prevailed numerically and quantitatively, comprising 39 and 35 methyl- and ethyl esters, respectively, in addition to 16 acetates as well as 3-methylbutyl hexanoate (64) and ethyl methyl propanedioate (81). Furthermore, 16 terpenes, nine alcohols, six γ- and δ-lactones, five aldehydes, four undecane hydrocarbons, and two furanones were tentatively identified. This qualitative composition of volatiles resembled that previously reported for fresh 'MD2' pineapples [4, 5, 19] and juice obtained thereof [20], except for some juice-specific constituents, such as free fatty acids and diverse nortriterpenoids, that were not found in the fresh-cut samples assessed herein.

Noteworthy, the concentrations of the volatiles reported in literature as the key odorants of pineapple [21], i.e., ethyl 2-methylpropanoate (no. 8, described to exert a fruity odour), methyl 2-methylbutanoate (11, fruity, apple-like), ethyl 2-methylbutanoate (15, fruity), and 4-hydroxy-2,5-dimethyl-3(2*H*)-furanone (127, sweet, pineapple-like, caramel-like) were found in elevated concentrations in the samples from fully ripe fruit compared to those obtained from green-ripe pineapples stored for 14 days prior to processing. Applying our analytical method, another key aroma compound of pineapples 1-(3*E*,5*Z*)-3,5-undecatriene (52b,

Table 1 Physicochemical characteristics of fresh-cut pineapple

	Fully ripe (AF) 2 dap	Fully ripe (AF) 5 dap	Fully ripe (AF) 8 dap	Green-ripe (SF) 2 dap	Green-ripe (SF) 5 dap	Green-ripe (SF) 8 dap
Drip loss (% w/w)	5.4 ± 1.0ab	6.1 ± 1.0ab	7.4 ± 1.6a	5.2 ± 0.5b	6.4 ± 0.2ab	7.2 ± 0.5ab
pH (–)	3.75 ± 0.09ab	3.76 ± 0.09ab	3.85 ± 0.08a	3.57 ± 0.07b	3.63 ± 0.09ab	3.64 ± 0.09b
TSS (°Brix)	10.50 ± 0.87a	10.90 ± 0.81ab	10.78 ± 0.29a	11.10 ± 1.94a	10.83 ± 1.91a	10.95 ± 1.80a
TA (g/100 g of FW)	0.39 ± 0.04b	0.40 ± 0.04b	0.36 ± 0.01b	0.53 ± 0.02a	0.50 ± 0.05a	0.52 ± 0.02a
TSS/TA (g/g)	27.9 ± 2.6ab	27.5 ± 2.8ab	29.9 ± 1.6a	21.2 ± 4.2b	22.1 ± 4.5b	21.1 ± 3.0b
(all- <i>E</i>)-β-Carotene (µg/100 g of FW)	37 ± 4a	33 ± 5a	38 ± 9a	34 ± 5a	30 ± 7a	34 ± 5a
Total carotenoids (µg/100 g of FW)	499 ± 72a	518 ± 72a	374 ± 96a	470 ± 63a	484 ± 24a	407 ± 39a
RAEs (µg RAE/100 g of FW)	3.1 ± 0.4a	2.7 ± 0.5a	3.2 ± 0.8a	2.9 ± 0.5a	2.5 ± 0.6a	2.8 ± 0.4a

Values represent means ± standard deviations ($n = 4$)

Different letters in one row indicate significant ($p < 0.05$) differences of means

Table 2 HS-SPME-GC-MS data of volatiles isolated from fresh-cut pineapple

No	Proposed identity	CAS-No	LRI DB-Wax	LRI HP-5ms	AF 2 dap	AF 5 dap	AF 8 dap	SF 2 dap	SF 5 dap	SF 8 dap	Criteria
1	Acetaldehyde	75-07-0	703	<500	–	0.29	0.31	–	0.12	0.16	MS, LRI _p
2	Methyl acetate	79-20-9	826	530	5.67	6.17	7.09	6.55	5.93	7.65	MS, LRI _p
3	Ethyl acetate	141-78-6	890	613	70.1	96.5	140	7.38	62.3	91.5	MS, LRI _p , LRI _{sp}
4	Methyl propanoate	554-12-1	910	627	4.70	4.77	7.14	2.63	2.90	4.15	MS, LRI _p , LRI _{sp}
5	Methyl 2-methylpropanoate	547-63-7	924	685	1.17	1.30	1.69	0.81	0.86	1.18	MS, LRI _p , LRI _{sp}
6	Ethanol	64-17-5	933	<500	11.7	27.7	52.2	1.16	14.0	27.5	MS, LRI _p
7	Ethyl propanoate	105-37-3	956	711	1.21	1.13	2.06	0.20	0.59	1.41	MS, LRI _p , LRI _{sp}
8	Ethyl 2-methylpropanoate	97-62-1	966	754	0.51	0.55	0.89	0.22	0.30	0.82	MS, LRI _p , LRI _{sp}
9	<i>n</i> -Propyl acetate	109-60-4	975	712	2.00	2.99	4.38	0.69	3.40	4.68	MS, LRI _p , LRI _{sp}
10ab	Methyl butanoate + ethyl 2-propenoate	623-42-7 140-88-5	990	719	34.2	31.1	34.1	29.4	21.9	21.2	MS, LRI _p , LRI _{sp}
11	Methyl 2-methylbutanoate	868-57-5	1013	772	59.9	62.4	78.2	55.1	49.6	57.3	MS, LRI _p , LRI _{sp}
12	Methyl 3-methylbutanoate	556-24-1	1019	–	3.21	3.39	4.14	1.59	1.74	2.30	MS, LRI _p
13	Ethyl butanoate	105-54-4	1035	801	10.9	14.7	24.7	0.66	6.09	13.9	MS, LRI _p , LRI _{sp}
14	<i>n. i.</i>	–	1043	–	0.09	0.28	0.94	–	0.13	0.22	–
15	Ethyl 2-methylbutanoate	7452-79-1	1050	846	18.2	17.2	26.3	1.29	8.11	21.6	MS, LRI _p , LRI _{sp}
16	Ethyl 3-methylbutanoate	108-64-5	1064	850	0.74	1.21	2.18	0.26	0.96	2.50	MS, LRI _p , LRI _{sp}
17	<i>n</i> -Butyl acetate	123-86-4	1069	814	0.32	0.48	0.60	0.17	0.34	0.36	MS, LRI _p , LRI _{sp}
18	Hexanal	66-25-1	1080	799	0.12	0.17	0.18	0.46	0.18	0.17	MS, LRI _p , LRI _{sp}
19	Methyl pentanoate	624-24-8	1085	821	4.23	3.25	2.92	4.10	2.45	2.06	MS, LRI _p , LRI _{sp}
20	2-Methylpropan-1-ol	78-83-1	1098	–	–	0.21	0.48	–	0.10	0.28	MS, LRI _p
21ab	Diethyl carbonate + methyl (<i>E</i>)-2-butenate	105-58-8 623-43-8	1105	783*	0.73	1.9	5.80	0.37	0.78	1.49	MS, LRI _p
22ab	2-/3-Methylbutyl acetate ^a	624-41-9 123-92-2	1118	874/881	14.9	54.7	129	1.89	32.1	124	MS, LRI _p , LRI _{sp}
23	Ethyl pentanoate	539-82-2	1132	901	3.39	4.44	7.36	0.25	1.74	2.99	MS, LRI _p , LRI _{sp}
24	β-Myrcene	123-35-3	1157	990	0.48	0.38	0.44	0.15	0.11	0.11	MS, LRI _p , LRI _{sp}
25	<i>n</i> -Pentyl acetate	628-63-7	1170	915	0.28	0.24	0.16	0.37	0.10	0.26	MS, LRI _p , LRI _{sp}
26	Methyl hexanoate	106-70-7	1190	925	481	319	318	370	175	155	MS, LRI _p , LRI _{sp}
27	Limonene	138-86-3	1199	1026	0.69	0.42	0.54	0.14	0.17	0.22	MS, LRI _p , LRI _{sp}
28ab	2-/3-Methylbutanol ^a	123-51-3 137-32-6	1210	730/733	0.53	1.50	4.19	0.22	0.32	1.97	MS, LRI _p , LRI _{sp}
29ab	Methyl 5-hexenoate + ethyl hexanoate	2396-80-7 123-66-0	1231	912	383	512	765	21.7	205	303	MS, LRI _p , LRI _{sp}
30	Methyl (<i>E</i>)-4-hexenoate	14017-81-3	1243	999	1.07	0.61	1.30	0.31	0.24	0.29	MS, LRI _p
31	(<i>E</i>)-β-Ocimene	3779-61-1	1247	1047	40.2	34.0	44.3	0.51	0.54	0.48	MS, LRI _p , LRI _{sp}
32	3-Methyl-2-butenylacetate	1191-16-8	1251	921	5.31	4.55	4.50	0.58	0.47	0.64	MS, LRI _p

Table 2 (continued)

No	Proposed identity	CAS-No	LRI DB-Wax	LRI HP-5ms	AF 2 dap	AF 5 dap	AF 8 dap	SF 2 dap	SF 5 dap	SF 8 dap	Criteria
33	Methyl (Z)-3-hexenoate	13894-62-7	1256	936	5.76	3.00	2.32	4.22	2.35	2.25	MS, LRI _p
34	Methyl (E)-3-hexenoate	2396-78-3	1261	938	7.03	4.15	3.50	5.22	2.48	2.19	MS, LRI _p
35	<i>p</i> -Cymene	99-87-6	1266	1022	0.12	–	0.14	–	0.03	0.03	MS, LRI _p , LRI _{sp}
36	<i>n</i> -Hexyl acetate	142-92-7	1270	1014	0.43	0.07	–	0.33	0.09	0.12	MS, LRI _p , LRI _{sp}
37	Ethyl 5-hexenoate	54653-25-7	1275	–	0.95	1.27	2.36	0.05	0.30	0.53	MS, LRI _p
38	α -Terpinolene	586-62-9	1280	–	0.22	0.18	0.25	0.02	0.02	0.05	MS, LRI _p
39	3-Hydroxybutan-2-one (acetoin)	513-86-0	1283	–	–	–	0.04	–	–	0.02	MS, LRI _p
40	Methyl heptanoate	106-73-0	1287	1024	6.35	3.33	4.75	2.02	0.99	0.99	MS, LRI _p
41	Methyl (E)-2-hexenoate	13894-63-8	1288	965	0.70	0.71	0.94	0.49	0.40	0.39	MS, LRI _p , LRI _{sp}
42	Ethyl (Z)-3-hexenoate	64187-83-3	1292	1006	0.17	0.21	0.63	–	0.06	0.12	MS, LRI _p , LRI _{sp}
43	Ethyl (E)-3-hexenoate	26553-46-8	1300	1010	3.05	3.06	3.77	0.15	2.24	3.72	MS, LRI _p , LRI _{sp}
IS	2-Methyl-1-pentanol (IS)	105-30-6	1306	833	IS	IS	IS	IS	IS	IS	MS, LRI _p , LRI _{sp}
44	(Z)-3-Hexen-1-ol acetate	3681-71-8	1315	–	5.49	1.23	0.59	0.23	0.10	0.10	MS, LRI _p
45ab	Methyl (Z)-4-heptenoate + ethyl heptanoate	39924-30-6 106-30-9	1331	1020* 1098	5.42	5.20	9.59	0.87	1.34	2.04	MS, LRI _p
46	Ethyl (E)-2-hexenoate	1552-67-6	1342	1043	0.45	0.95	1.14	–	0.23	0.37	MS, LRI _p , LRI _{sp}
47	1-Hexanol	111-27-3	1354	865	–	–	–	–	–	0.10	MS, LRI _p , LRI _{sp}
48	4-Hydroxy-4-methylpentan-2-one (diacetone alcohol)	123-42-2	1361	–	0.37	0.30	0.29	0.36	0.45	0.48	MS, LRI _p
49	Ethyl (Z)-4-heptenoate*	39924-27-1	1376	–	0.59	0.74	0.95	0.20	0.44	0.62	MS, LRI _p
50	n. i.	–	1379	–	0.90	0.51	0.55	0.31	0.15	0.13	–
51	n. i.	–	1381	–	0.83	0.68	0.71	0.56	0.31	0.37	–
52abc	Methyl octanoate + 1-(3E,5Z)-3,5-undecatriene + nonanal	111-11-5 447-08-6 124-19-6	1390	1125 1173 1106	49.6	26.7	38.0	9.73	6.64	7.03	MS, LRI _p , LRI _{sp} MS, LRI _p , LRI _{sp} MS, LRI _p , LRI _{sp}
53	Methyl 2-hydroxy-3-methylbutanoate	17417-00-4	1398	–	0.29	0.32	0.43	0.16	0.17	0.25	MS, LRI _p
54	1-(3E,5E)-3,5-Undecatriene	19883-29-5	1400	1182	0.13	0.12	0.23	0.02	0.02	0.02	MS, LRI _p , LRI _{sp}
55	Methyl 2-(methylthio)acetate	16630-66-3	1402	910	0.35	0.25	0.29	0.17	0.20	0.20	MS, LRI _p , LRI _{sp}
56	n. i. (<i>m/z</i> 204)	–	1411	–	2.40	1.73	2.68	0.39	0.27	0.29	–
57	Methyl (Z)-4-octenoate*	21063-71-8	1415	1115	0.70	0.55	0.74	0.24	0.22	0.29	MS, LRI _p , LRI _{sp}
58	Ethyl 2-hydroxy-3-methylbutanoate	2441-06-7	1423	–	0.13	0.56	1.20	0.13	0.22	0.48	MS, LRI _p
59	Methyl (Z)-5-octenoate*	41654-15-3	1429	–	20.8	13.6	15.4	10.1	6.51	7.25	MS, LRI _p
60	Ethyl octanoate	106-32-1	1433	1198	42.0	41.9	76.9	1.65	7.61	12.7	MS, LRI _p , LRI _{sp}
61	Ethyl 2-(methylthio)acetate	4455-13-4	1441	984	0.47	0.61	0.81	0.11	0.27	0.47	MS, LRI _p , LRI _{sp}
62	1,3,5,8-Undecatetraene (1) ^b	50277-31-1	1446	1176*/1186*	3.36	2.94	3.57	0.17	0.26	0.28	MS, LRI _p
63	Methyl (E)-3-octenoate	35234-16-3	1453	1130*	0.77	0.41	0.54	0.37	0.33	0.41	MS, LRI _p
64	3-Methylbutyl hexanoate	2198-61-0	1456	1250	–	–	0.28	–	–	0.17	MS, LRI _p , LRI _{sp}

Table 2 (continued)

No	Proposed identity	CAS-No	LRI DB-Wax	LRI HP-5ms	AF 2 dap	AF 5 dap	AF 8 dap	SF 2 dap	SF 5 dap	SF 8 dap	Criteria
65ab	1,3,5,8-Undecateraene (2) ^b +ethyl (Z)-4-octenoate*	50277-31-1 34495-71-1	1462	1176*/1186* 1189	0.76	0.78	1.32	0.24	0.32	0.53	MS, LRI _p MS, LRI _p , LRI _{sp}
66	n. i. (<i>m/z</i> 204)	–	1470	–	0.57	0.41	0.64	0.13	0.13	0.19	–
67	Ethyl (Z)-5-octenoate*	72820-74-7	1473	–	12.5	16.2	23.0	0.81	6.47	10.5	MS, LRI _p
68	Ethyl hexadienoate (unknown isomer)	2396-84-1	1479	1094*	0.11	0.10	0.20	–	0.03	0.11	MS, LRI _{sp}
69	α-Copaene	3856-25-5	1482	1385	6.52	4.41	6.76	1.13	0.84	0.92	MS, LRI _p , LRI _{sp}
70	erythro-Butane-2,3-diol diacetate	17998-02-6	1485	1062*	0.27	0.10	0.06	0.15	0.07	0.08	MS, LRI _p
71	Methyl nonanoate	1731-84-6	1490	1224	0.36	0.35	0.37	0.11	0.08	0.12	MS, LRI _p , LRI _{sp}
72ab	Decanal + ethyl (E)-3-octenoate	112-31-2 1117-65-3	1492	1204	0.68	1.03	1.34	0.67	0.90	1.20	MS, LRI _p , LRI _{sp} MS, LRI _p
73	Methyl (E)-2-octenoate	7367-81-9	1494	1170*	0.37	0.29	0.23	0.15	0.05	0.05	MS, LRI _p
74	Dimethyl propanedioate	108-59-8	1507	929*	7.22	6.99	6.29	8.25	6.83	6.89	MS, LRI _p , LRI _{sp}
75	Benzaldehyde	100-52-7	1512	957	0.14	0.18	0.18	0.04	0.05	0.08	MS, LRI _p , LRI _{sp}
76	Ethyl 3-hydroxybutanoate	5405-41-4	1513	–	0.32	0.85	1.67	0.19	0.47	1.36	MS, LRI _p
77	Methyl 3-(methylthio)propanoate	13532-18-8	1518	1024	240	200	216	127	102	103	MS, LRI _p , LRI _{sp}
78	threo-Butane-2,3-diol diacetate	79297-93-1	1524	1078*	0.66	0.64	0.92	0.24	0.29	0.60	MS, LRI _p
79	Methyl 3-acetoxy-2-methylbutanoate, DS1	139564-42-4	1525	1085*	6.85	6.15	7.99	2.34	2.28	2.92	MS, LRI _p
80	Ethyl nonanoate	123-29-5	1534	–	0.33	0.24	0.48	–	0.03	0.09	MS, LRI _p
81	Methyl 3-acetoxybutanoate*	89422-42-4	1536	1040*	2.80	2.56	2.50	1.49	1.20	1.22	MS, LRI _p
82	Ethyl methyl propanedioate	6186-89-6	1540	–	2.16	3.84	5.34	0.17	2.09	3.46	MS, LRI _p
83	2,3-Butanediol	513-85-9	1542	–	0.34	1.42	3.58	0.17	0.78	2.44	MS, LRI _p
84ab	Linalool + ethyl (E)-2-octenoate	78-70-6 7367-82-0	1549	1099	0.67	0.75	1.86	0.17	0.14	0.23	MS, LRI _p , LRI _{sp} MS, LRI _p
85	Methyl 3-acetoxy-2-methylbutanoate, DS2	139564-42-4	1554	1099*	1.11	0.89	1.11	0.18	0.12	0.19	MS, LRI _p
86ab	Ethyl 3-(methylthio)propanoate + ethyl 3-acetoxy-2-methylbutanoate, DS1	13327-56-5 139564-43-5	1560	1100 1153*	111	153	301	3.52	44.2	83.6	MS, LRI _p , LRI _{sp} MS, LRI _p
87	n. i.	–	1563	–	1.13	0.80	0.83	0.34	0.31	0.41	–
88	n. i.	–	1570	–	0.57	0.41	0.31	0.31	0.22	0.21	–
89ab	Methyl 2-hydroxyhexanoate + diethyl propanedioate*	68756-64-9 105-53-3	1575	– 1073	0.89	1.26	2.42	0.21	0.44	1.61	MS, LRI _p MS, LRI _p , LRI _{sp}
90	β-Elementene	515-13-9	1578	1391	1.96	1.33	2.04	0.34	0.26	0.26	MS, LRI _p , LRI _{sp}
91	4-methoxy-2,5-dimethyl-3(2H)-furanone	4077-47-8	1586	1059	37.9	36.5	43.6	9.72	6.95	10.4	MS, LRI _p , LRI _{sp}
92	Ethyl 3-acetoxy-2-methylbutanoate, DS2	139564-43-5	1588	1165*	–	–	–	–	–	0.36	MS, LRI _p
93	Methyl decanoate	110-42-9	1591	1324	3.20	2.07	3.20	0.51	0.37	0.45	MS, LRI _p , LRI _{sp}
94	1-Terpinen-4-ol	562-74-3	1598	1183	1.58	1.60	1.80	0.60	0.54	0.59	MS, LRI _p , LRI _{sp}
95	n. i. (<i>m/z</i> 204)	–	1602	–	0.99	0.68	0.97	0.21	0.14	0.16	–

Table 2 (continued)

No	Proposed identity	CAS-No	LRI DB-Wax	LRI HP-5ms	AF 2 dap	AF 5 dap	AF 8 dap	SF 2 dap	SF 5 dap	SF 8 dap	Criteria
96	n. i.	–	1608	–	0.70	0.63	0.90	0.24	0.25	0.40	–
97	Methyl benzoate	93-58-3	1611	–	0.45	0.40	0.55	0.25	0.29	0.48	MS, LRI _p
98	n. i.	–	1616	–	–	–	0.40	–	–	0.20	–
99ab	Methyl (Z)-4-decenoate + 3-(methylthio)propyl acetate	7367-83-1 16630-55-0	1621	1308	10.5	6.25	7.54	3.10	2.57	4.29	MS, LRI _p , LRI _{sp} MS, LRI _p
100ab	Methyl 4-(methylthio)butanoate + ethyl methyl butanedioate	6186-89-6	1632	–	0.15	0.38	0.68	0.11	0.15	0.34	MS, LRI _p MS, LRI _p
101	Ethyl decanoate	110-38-3	1636	1395	3.23	3.56	6.91	0.23	0.64	1.02	MS, LRI _p , LRI _{sp}
102	Methyl 3-hydroxyhexanoate	21188-58-9	1645	1051	0.77	0.73	1.05	0.23	0.17	0.24	MS, LRI _p , LRI _{sp}
103	n. i. (<i>m/z</i> 204)	–	1648	–	0.90	0.75	0.88	0.15	0.16	0.25	–
104	Ethyl (Z)-4-decenoate	7367-84-2	1663	1379	7.63	7.68	14.5	0.66	2.80	4.67	MS, LRI _p , LRI _{sp}
105	Diethyl butanedioate	123-25-1	1674	–	–	–	1.04	–	0.09	0.42	MS, LRI _p
106	α-Amorphene	23515-88-0	1676	1476	2.10	2.13	3.32	0.79	0.67	0.98	MS, LRI _p , LRI _{sp}
107	Ethyl 3-hydroxyhexanoate	2305-25-1	1679	1128	3.09	2.52	2.24	0.64	0.33	0.31	MS, LRI _p
108	Methyl 3-acetoxyhexanoate	21188-60-3	1682	1207*	40.9	26.7	32.7	11.6	7.61	9.13	MS, LRI _p
109	γ-Hexalactone	695-06-7	1686	1053	1.99	2.97	3.87	2.09	1.73	2.29	MS, LRI _p , LRI _{sp}
110	α-Gurjunene	489-40-7	1694	1409	1.37	1.12	1.44	0.24	0.18	0.24	MS, LRI _p , LRI _{sp}
111	β-Selinene	17066-67-0	1703	1488	0.25	–	–	0.06	0.09	0.10	MS, LRI _p , LRI _{sp}
112	α-Selinene	473-13-2	1708	1494	0.22	0.13	0.22	0.03	–	–	MS, LRI _p , LRI _{sp}
113ab	α-Murolene + 3-(methylthio)propanol	31983-22-9 505-10-2	1717	1500	2.14	1.66	2.61	0.37	0.32	0.49	MS, LRI _p , LRI _{sp} MS, LRI _p
114ab	Ethyl 3-acetoxyhexanoate + benzyl acetate	21188-61-4 140-11-4	1720	1276* 1164	103	29.4	52.0	1.21	8.65	15.5	MS, LRI _p MS, LRI _p , LRI _{sp}
115	Methyl 4-acetoxyhexanoate*	112059-09-3	1727	1168*	6.76	3.82	3.86	0.79	0.39	0.40	MS, LRI _p
116	δ-Cadinene	483-76-1	1744	1523	1.13	0.84	1.01	0.34	0.21	0.28	MS, LRI _p , LRI _{sp}
117	Methyl 2-phenylacetate	101-41-7	1750	1178	0.92	0.90	0.95	0.78	0.74	0.85	MS, LRI _p , LRI _{sp}
118	Ethyl 4-acetoxyhexanoate*	121308-81-4	1765	1301*	2.97	2.75	4.53	–	0.93	1.16	MS, LRI _p
119	Methyl 5-acetoxyhexanoate	35234-22-1	1769	1254*	26.1	18.2	21.4	2.98	1.71	1.73	MS, LRI _p
120	δ-Hexalactone	823-22-3	1773	1097	0.78	0.50	0.56	0.15	0.09	0.10	MS, LRI _p
121	Ethyl 2-phenylacetate	101-97-3	1778	1245*	1.56	1.5	2.60	0.85	0.42	0.90	MS, LRI _p
122ab	Ethyl 5-acetoxyhexanoate + 2-phenylethyl acetate	35234-24-3 103-45-7	1805	1322* 1257	3.61	2.88	6.29	0.08	0.33	0.69	MS, LRI _p MS, LRI _p , LRI _{sp}
123	p-Cymenol	1197-01-9	1846	1175	0.20	–	–	0.14	0.16	0.23	MS, LRI _p , LRI _{sp}
124	γ-Octalactone	104-50-7	1899	1258	3.21	2.58	3.78	0.75	0.58	0.88	MS, LRI _p , LRI _{sp}
125	2-Phenylethanol	60-12-8	1904	–	–	–	–	–	–	0.05	MS, LRI _p
126	δ-Octalactone	698-76-0	1949	1290	1.55	1.39	2.10	0.30	0.23	0.31	MS, LRI _p , LRI _{sp}

Table 2 (continued)

No	Proposed identity	CAS-No	LRI DB-Wax	LRI HP-5ms	AF 2 dap	AF 5 dap	AF 8 dap	SF 2 dap	SF 5 dap	SF 8 dap	Criteria
127	4-Hydroxy-2,5-dimethyl-3(2H)-furanone	3658-77-3	2030	1051	2.01	1.61	3.19	0.12	0.13	0.25	MS, LRI _p
128	Methyl cinnamate	103-26-4	2058	1384	–	–	–	–	0.04	0.05	MS, LRI _p , LRI _{sp}
129	Ethyl cinnamate	103-36-6	2111	–	–	–	0.38	–	0.05	0.16	MS, LRI _p
130	γ-Decalactone	706-14-9	2120	1473	0.55	0.50	0.67	0.12	0.12	0.18	MS, LRI _p
131	δ-Decalactone	705-86-2	2163	1502	0.49	0.45	0.92	0.15	0.14	0.20	MS, LRI _p

Means ($n=4$) were expressed in μg 2-methyl-1-pentanol equivalents per 100 g of pineapple flesh determined using a polar DB-Wax stationary phase

DS diastereomers, IS internal standard, LRI_p linear retention index on a polar polyethylene glycol stationary phase (DB-Wax), LRI_{sp} linear retention index on a slightly polar 5%-phenyl-95%-methylpolysiloxane stationary phase (HP-5ms), MS electron impact mass spectrum, $n. i.$ not identified (m/z 204 indicates a sesquiterpene)

*Tentatively assigned

^a2- and 3-methylbutyl acetate (no. 22ab) and the corresponding alcohols 2- and 3-methylbutanol (no. 28ab) were not resolved on the DB-Wax but separated on the HP-5ms stationary phase

^bTwo 1,3,5,8-undecatriene isomers detected on the HP-5 ms stationary phase cannot be unambiguously assigned to the two isomers with LRI_p 1446 and 1462

fresh, pineapple-like) was not baseline resolved from the abundant ester methyl octanoate and thus, could not be quantitated separately. Moreover, γ - and δ -octalactone (124 and 126, resp.) that have been proposed to exert the distinct coconut-like odour in fully ripe pineapples [22] were found in elevated concentrations in the AF samples compared to those in the SF fresh-cut produce.

Unsupervised classification by PCA and HCA

The effect of harvest maturity and post-harvest procedures on fresh-cut pineapple volatiles was assessed by PCA. The scores and correlation loadings obtained for the first two principal components (PCs) are displayed in Fig. 1a, a'. PC1 and PC2 of the model explained high 80% of variance. PC1 (60%) clearly segregated the fresh-cut samples obtained from green-ripe pineapples after mimicked sea freight (SF) from a second cluster comprising the air-freighted (AF) produce. In addition, the samples were arranged along PC2 (20%) according to the days after processing. This clustering was also observed in the HCA as illustrated by Fig. 1b and the corresponding circles in the PCA scores plot, respectively.

The most discriminative volatiles contributing to the clustering by PCA are compiled in Table 3. Hereby, volatiles with positive loadings on PC1 contribute to the differentiation of the two principal fresh-cut categories, i.e., SF and AF produce. In general, elevated concentrations of volatiles were found in the samples from fully ripe fruit compared to those from their sea-freighted counterparts as can be deduced from the arrangement of the loadings on the right part of the plot. Moreover, two sub-groups of volatiles can be distinguished. Whereas those with positive loadings on PC2, i.e., diverse methyl esters of intermediate chain fatty acids (C6–C10), such as methyl 5-acetoxylhexanoate (119), methyl heptanoate (40), methyl octanoate (52a), methyl (*Z*)-5-octanoate (59), and methyl decanoate (93), were correlated to the freshly processed samples, volatiles with negative loadings on PC2 contributed to the segregation of the stored produce. In particular, ethanol (6) and diverse ethyl esters of short to intermediate chain fatty acids (C2–C7), such as *inter alia* ethyl acetate (3), ethyl butanoate (13), ethyl pentanoate (23), ethyl hexanoate (29b), and ethyl (*Z*)-4-heptenoate (49), were found among the markers contributing to the clustering of the progressed storage stages. Further discriminative volatiles segregating the latter samples were assigned to ethyl esters, i.e., ethyl 3-hydroxybutanoate (76), ethyl methyl propanedioate (82) and the sulphurous volatile ethyl 3-(methylthio)propanoate (86a). The latter was not baseline resolved from the unique pineapple constituent ethyl 3-acetoxy-2-methylbutanoate (86b) [13] on a PEG stationary phase.

Fig. 1 PCA scores (**a**) and loadings plot (**a'**) illustrating the effect of harvest maturity and storage duration on fresh-cut pineapple volatiles. The large circles represent the clusters obtained by HCA (**b**). *dap* days after processing, *AF* fresh-cut samples from fruit harvested at

a full maturity (“air freight”), *SF* fresh-cut produce from green-ripe fruit stored for 14 days prior to processing (“sea freight”). Loadings of tentative markers are highlighted by filled circles and labelled with the compound numbers compiled in Table 3

In summary, methyl esters prevailed in the fresh samples, whereas diverse ethyl esters were generated with progressing storage duration. This shift from methyl to ethyl esters has been previously observed during post-harvest storage of

pineapple fruit and may be triggered by the endogenous and possibly microbial genesis of ethanol [4]. Noteworthy, the differences in the volatiles between fully ripe fruit and those harvested at a green-ripe stage following chilled storage for

Table 3 Tentative marker compounds identified via PCA

No.	Identity	PC 1 (60%) ^a	PC 2 (20%) ^b
13	Ethyl butanoate	0.099	− 0.091
52abc	Methyl octanoate + 1-(3 <i>E</i> ,5 <i>Z</i>)-3,5-undecatriene + nonanal	0.096	0.098
6	Ethanol	0.087	− 0.124
119	Methyl 5-acetoxylhexanoate	0.098	0.089
40	Methyl heptanoate	0.089	0.113
59	Methyl (Z)-5-octenoate	0.085	0.123
93	Methyl decanoate	0.105	0.064
23	Ethyl pentanoate	0.105	− 0.064
82	Ethyl methyl propanedioate	0.089	− 0.109
3	Ethyl acetate	0.092	− 0.103
29ab	Methyl 5-hexenoate + ethyl hexanoate	0.107	− 0.057
86ab	Ethyl 3-(methylthio)propanoate + ethyl 3-acetoxy-2-methylbutanoate, DS1	0.107	− 0.056
49	Ethyl (Z)-4-heptenoate	0.101	− 0.074

DS diastereomer

^aSignals with positive loadings on PC1 contribute to the discrimination of sea-freighted (SF) and air-freighted samples (see Fig. 1a, a')

^bSignals with positive loadings on PC2 are correlated to the fresh samples, those with negative to the stored produce (see Fig. 1a, a')

14 days were largely retained throughout the entire storage period. To further explore the particular effect of post-processing storage, a PLS regression was calculated as discussed in the following section.

PLS regression

The scores and correlation loadings obtained for the first two latent variables (LVs) of the PLS regression model are illustrated in Fig. 2. As also observed in the PCA, the samples are arranged in two clusters comprising the air-freighted products and those obtained from green-ripe pineapples after mimicked sea freight. In addition, the model clearly fitted an effect of storage as indicated by the high 98% of cumulative variance in the *y*-variable explained by LV1 ($Y=79\%$) and LV2 ($Y=19\%$), as well as by the length of the correlation loadings vector.

Variable identification (VID) coefficients revealed distinctive volatiles (Table 4). Hereby, positive VIDs indicate the genesis of the respective compound with progressing storage duration. In most instances, such volatiles were alcohols deriving from fermentative metabolic pathways, i.e., ethanol (6), 2-methylpropanol (20), 2-/3-methylbutanol (28ab), and 2,3-butanediol (83). Moreover, the acetates *n*-propyl acetate (9) and 2-/3-methylbutyl acetate (22ab) in addition to diverse ethyl esters, e.g., ethyl 3-methylbutanoate (16), ethyl 2-hydroxy-3-methylbutanoate (58), and diethyl butanedioate (105) were found as possible markers generated with progressing storage. Vice versa, the concentrations of the volatiles with negative VIDs, here methyl pentanoate (19), methyl (Z)-3-hexenoate (33), and *n*-hexyl acetate (36)

Fig. 2 PLS regression illustrating the effect of storage on fresh-cut pineapple volatiles. Volatiles with $VID \geq |0.80|$ are displayed as filled circles and labelled with the peak numbers compiled in Table 4

decreased during storage. This may be attributed to transesterification reactions or possibly the enzymatic cleavage of certain esters during storage of fresh-cut pineapples as previously described by Lamikanra [7]. Interestingly, 2,3-butanediol (83) that was found as a putative storage marker of fresh-cut produce represents a precursor of *threo*- and *erythro*-2,3-butanediol diacetate that have been reported to arise during post-harvest storage of green-ripe pineapples [4,

Table 4 Discriminative volatiles ($VID \geq 0.80$) indicating the effect of storage on fresh-cut pineapples identified via PLS regression

No.	Identity	VID ^a
22ab	2-/3-Methylbutyl acetate	0.94
76	Ethyl 3-hydroxybutanoate	0.94
83	2,3-Butanediol	0.93
20	2-Methylpropan-1-ol	0.91
9	<i>n</i> -Propyl acetate	0.91
16	Ethyl 3-methylbutanoate	0.87
6	Ethanol	0.85
64	3-Methylbutyl hexanoate	0.84
58	Ethyl 2-hydroxy-3-methylbutanoate	0.81
98	<i>n. i.</i>	0.81
105	Diethyl butanedioate	0.81
28ab	2-/3-Methylbutanol	0.80
19	Methyl pentanoate	−0.81
33	Methyl (<i>Z</i>)-3-hexenoate	−0.83
36	<i>n</i> -Hexyl acetate	−0.85

n. i. not identified

^aPositive variable identification (*VID*) coefficients indicate the genesis of the volatiles. Vice versa, negative *VID* coefficients indicate diminishing concentrations with progressing storage duration (see also Fig. 2 and concentrations compiled in Table 2)

13]. Most of the aforementioned volatiles may derive from endogenous metabolic pathways, but also from microbial growth that was assessed in the second part of this study.

Microbiological analysis

To further characterise the influence of post-harvest procedures on the quality of fresh-cut pineapples, total plate counts (TPCs), pseudomonads, *Enterobacteriaceae*, and the yeast and mould counts were assessed. *Enterobacteriaceae* were not detected across all samples (not shown in Fig. 3).

With progressing storage duration, the TPCs increased in both fresh-cut categories (Fig. 3a). However, the TPCs determined in the air-freighted products (AF 3.3–4.4 log₁₀ CFU/g) were significantly smaller than those in their counterparts obtained from pineapples after mimicked sea freight (SF 4.6–6.5 log₁₀ CFU/g). Compared to the TPCs, *Pseudomonas* spp. viable counts were found at lower levels of 3.2–3.5 log₁₀ CFU/g (AF) and 3.2–4.1 log₁₀ CFU/g (SF) as determined across all air- and sea-freighted samples, respectively. In both sample categories, the pseudomonads only slightly increased during storage (Fig. 3b).

Whereas the initial TPC already differed comparing the AF and SF samples, comparable yeast and mould counts of 3.4 and 3.6 log₁₀ CFU/g, respectively, were found in the two fresh-cut categories assessed 2 dap (Fig. 3c). However, with progressing storage, the yeasts and moulds significantly increased and the plate counts of the sea-freighted samples

Fig. 3 Total plate count, TPCs (a), pseudomonads (b), and yeast and mould counts (c) in fresh-cut pineapples displayed as log₁₀ CFU/g. *Enterobacteriaceae* were not detected among all samples assessed (data not shown). Different letters indicate significant ($p < 0.05$) differences of means. The dashed line indicates the maximum acceptable plate count for fresh-cut fruit of 6.0 log₁₀ CFU as specified by the IFST [23]

(SF 5.6 and 6.5 log₁₀ CFU/g as determined 5 and 8 dap, respectively) clearly exceeded those of the air-freighted produce (AF 4.4 and 5.4 log₁₀ CFU/g, resp.).

Yeasts and moulds have been reported to be the most important spoilage microorganisms of fresh-cut fruits [23]. According to the Institute of Food Science and Technology (IFST) [23], the maximum acceptable plate count of 6.0 log₁₀ CFU/g shall not be exceeded during the entire shelf

life of sliced fruits stored under chilled conditions. All AF samples assessed displayed microbial loads smaller than $6.0 \log_{10}$ CFU/g, whereas the TPC as well as the yeast and mould count determined in the SF pineapples exceeded this critical value already five and eight days after processing, respectively (see dashed line in Fig. 3). Noteworthy, the pineapple flesh is not sterile and contains fungi, yeasts, and bacteria [24]. Storage of the green-ripe pineapples prior to processing may result in the elevated TPCs observed in the SF samples, possibly from the growth of this genuine microflora. Concluding, processing freshly harvested pineapples at full maturity resulted in lower total plate as well as yeast and mould counts compared to samples from the green-ripe fruit that were stored for 14 days prior to processing.

Conclusion

With the exception of the drip loss, the titratable acids, and the TSS/TA ratio, post-harvest procedures had only a marginal impact on the physicochemical properties of fresh-cut pineapples. By contrast, processing fully ripe pineapples resulted in lower total plate as well as yeast and mould counts compared to samples from green-ripe fruit stored for 14 days prior to processing. Consequently, processing fully ripe pineapples immediately after harvest may be recommended for fresh-cut processors targeting the premium market rather than using sea-freighted fruit. Moreover, HS-SPME–GC–MS analysis of volatiles allowed the unambiguous distinction between fresh-cut products obtained from fruit harvested at full maturity and green-ripe pineapples stored for 14 days mimicking their sea freight export.

In most instances, elevated concentrations of volatiles were found among the products from fully ripe pineapples. With progressing storage duration, additional volatiles deriving from fermentative metabolic pathways, i.e., diverse alcohols and ethyl esters, were generated.

Concluding, in particular the factors determining the sensory properties, i.e., TSS/TA and the aroma-determining volatiles were the most distinctive traits to discriminate air-freighted fresh-cut pineapples from the produce obtained from sea-freighted fruit. Hence, air-freighted fresh-cut produce may be recommended for consumers that desire to experience the unique aroma quality of fully ripe pineapples. The differing composition of volatiles indicates distinct sensory properties of the two fresh-cut categories assessed that may be subject of ongoing research.

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Declarations

Conflict of interest The authors declare no conflict of interest.

Compliance with ethics requirements This article does not contain any studies with human or animal subjects.

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