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Comprehensive chocolate aroma characterization in beverages containing jackfruit seed flours and cocoa powder

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ABSTRACT

Jackfruit (*Artocarpus heterophyllus* Lam) occurs abundantly in Brazil, but its seeds are often underutilized in food nutrition. Previously, we showed that roasted jackfruit seeds are an innovative source of chocolate aroma. In this study, we characterized the volatile content of experimental beverages containing jackfruit seed flours as compared to non-alkaline cocoa powder. The three key results of this study were that (i) the fermented jackfruit seed flour beverage (FJSBev) was similar to the non-alkaline cocoa powder beverage (CTRLBev); (ii) similar volatile groups (acids, alcohols, aldehydes, ester, furans, and pyrazines) were identified in the samples (FJSBev and CTRLBev); (iii) the beverages contained volatile compounds with a low threshold of cocoa attributes (butter, cocoa, coffee, floral, fruit, green, honey, mushroom, nut, and roasted). To conclude, the beverage formulation containing fermented jackfruit seeds had more volatile compounds and odor-active constituents than that with non-alkaline cocoa powder. Collectively, our data demonstrate that fermentation is critical to producing a chocolate aroma. Fermented jackfruit seed flours could be used as a partial or total additive to improve chocolate aroma in food formulations.

1. Introduction

Jackfruit (*Artocarpus heterophyllus* Lam) occurs abundantly in the wild and is popular in tropical countries. While the flesh is more often consumed, jackfruit seeds - which account for 18–25% of the fruit weight (Mahanta and Kalita, 2015) - are usually discarded as a waste stream (John and Narasimham, 1993; Kee and Saw, 2010). Recent evidence has suggested that jackfruit seeds have a great potential to be used sustainably by local communities in Brazil due to their favorable sensory attributes (Spada et al., 2017,2021).

Spada et al. (2017) showed that when jackfruit seeds are fermented and roasted like cocoa beans, a distinctive chocolate aroma develops. More recently, Spada et al. (2021) observed pyrazine synthesis (odor-active volatiles) in jackfruit seed flours depending on amino acid composition and sugar bioavailability during fermentation. Pyrazines are dominant odor-active compounds in roasted jackfruit seed flours, cocoa beans, and cocoa powder (Afoakwa, 2010; Al-Duais et al., 2009; Tran et al., 2015). The tetramethylpyrazine content is six-fold greater in cocoa powder compared to cocoa beans (Al-Duais et al., 2009).

Maillard reactions occur under alkaline conditions when amine groups increase their reactivity to reducing sugars (Perez-locas and Yaylayan, 2010). A pH difference as low as 0.4–0.5 can be responsible for a quantitative variation in the volatile composition (Al-Duais et al., 2009; Crafack et al., 2014). Bispo et al. (2002) studied the differences in pyrazine composition between alkaline and non-alkaline cocoa beans. The authors observed an increase in 2,3 dimetrylpyrazine and trimethylpyrazine content in alkaline cocoa, whereas a similar concentration of methylpyrazine, 2,5 dimethylpyrazine, and tretramethylpyrazne was identified in both alkaline and non-alkaline cocoa beans. Volatile compounds are the main factors contributing to the acceptability of cocoa products and encouraging their intake (Kowalska et al., 2020).

The presence of odor-active volatiles in food formulations results from the interaction between flavor compounds and other nonvolatile ingredients (Guichard, 2002), and from cooking modifications. In our study, we produced experimental beverages containing jackfruit seed flours to provide additional evidence on developing a chocolate aroma from jackfruit seeds. A non-alkaline cocoa powder beverage was developed under similar conditions and served as a control. Sioriki et al. (2021) showed that alkalization affects color, flavor, and aromatic compounds, probably due to accelerated oxidation of alcohols to ketones. Although Spada et al. (2017) showed that jackfruit seed flours could have coffee as an odor-active constituent, according to consumers and trained panelists, the formulations did not contain coffee in

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their composition. More recently, trained panelists detected a roasted odor in roasted jackfruit seed flours (Spada et al., 2021).

Spada et al. (2018) incorporated jackfruit seed flours into cappuccino formulations and concluded that cappuccinos could be produced with 50% and 75% cocoa replacement if fermented and dry jackfruit seed flours are used, respectively. The consumers' acceptance of the experimental cappuccinos was not significantly affected.

Given the innovative potential to produce chocolate aroma from jackfruit waste, this study characterized the volatile content of experimental beverages containing dry and fermented jackfruit seed flours compared to non-alkaline cocoa powder. This is the first study reporting the detection and tentative identification of chocolate volatiles in beverage formulations with low cocoa and no coffee ingredients added.

2. Materials and methods

2.1. Chemicals

2,3,5-trimethylpyrazine (≥ 99%), 1,2-dichlorobenzene (99%), and the alkane standards C7−C30 (>90%) were purchased from Sigma-Aldrich Química, São Paulo, Brazil.

2.2. Jackfruit samples

Thirty jackfruits (*Artocarpus heterophyllus* Lam, hard fruit variety) were manually collected from a single tree between December 2018 and January 2019 in the countryside of São Paulo, Brazil. Ripe fruits (yellow peel) 6 ± 2 kg were harvested. The samples were rinsed with water, and seeds were removed and submitted to drying (DJS -dry jackfruit seeds) or fermentation before roasting to obtain dry and fermented (FJS -fermented jackfruit seeds). For each treatment, seeds from eight to ten jackfruits were pooled, treated, and dried in four 1.5 kg batches, as described below. Fifty grams of each of the four batches were pooled (200 g) and roasted.

2.3. Seed processing

To obtain DJS samples, jackfruit seeds were dried in an oven at 60 °C with air circulation. After 24 h, spermoderms were manually removed, and the seeds remained for an additional 24 h in the same oven at the same temperature. To obtain FJS samples, we simulated the cocoa processing, as previously described (Spada et al., 2017). On the three first days, boxes were closed to promote anaerobic fermentation and then opened for 2 days.

2.4. Roasting and grinding

For each treatment, seed batches (200 g) were roasted in a rotary electric oven (laboratory sample roaster, Emmerich am Rhein, Germany) with digital temperature control. Seeds were roasted following the temperature protocol described by Spada et al. (2017). DJS samples were roasted at 171 (± 1) °C for 47 min and FJS samples were roasted at 154(± 1) °C for 35 min. Seeds were not heated during hammer milling to minimize the loss of volatile compounds. Flours were vacuum packed and stored protected from light at 8 (±1) °C. The Brazilian Industry of Cocoa (Rio das Pedras, São Paulo) provided alkaline cocoa powder (BRB 1300 HQ 26918P003) and natural non-alkaline cocoa powder (IBB 1100 HQ 32318P001) to serve as controls.

2.5. Powder beverage formulations

Beverage formulations were prepared following the recommendations of Spada et al. (2018). The authors suggest 50% and 75% cocoa replacement in DJS and FJS-added beverages, respectively. Accordingly, we developed three powder beverages, as follows (Table 1): a control beverage containing 25% non-alkaline cocoa powder (CTRLBev); an experimental beverage containing 12.5% FJS and 12.5% cocoa powder (FJSBev), and an experimental beverage containing 18.75% DJS and 6.25% cocoa powder (DJSBev). Twenty grams of powder were used for each 100 mL. The Brazilian Industry of Cocoa provided natural non-alkaline cocoa powder. The other ingredients (powdered sugar, powdered milk, sodium bicarbonate, cinnamon powder, soy lecithin, and xanthan gum) were bought at a local market.

Table 1
Control and experimental beverage formulations.

Ingredients (%)	CTRLBev	FJSBev	DJSBev
Jackfruit seed flour	0	12.5	18.75
Cocoa powder	25.0	12.5	6.25
Powdered sugar**	41.5	41.5	41.5
Powdered milk	30.35	30.35	30.35
Sodium bicarbonate	1.75	1.75	1.75
Powdered cinnamon	0.4	0.4	0.4
Soy lecithin	0.5	0.5	0.5
Xanthan gum	0.5	0.5	0.5
Total	100	100	100

**supplemented with 2% corn starch. CTRLBev = control formulation containing non-alkaline cocoa powder; FJSBev = beverage formulation containing fermented jackfruit seed flour; DJSBev = beverage formulation containing dry jackfruit seed flour.

2.6. Physicochemical characterization

2.6.1. Moisture

The moisture content of the samples was determined by a standard gravimetric method using infrared light (Bel Engineering Model B-TOP-Ray).

2.6.2. Color

Color parameters (CIE-lab L*, a*, and b* scale) were measured in a Minolta colorimeter with illuminant C, which was previously calibrated on a white surface ($Y = 93.7$, $x = 0.3135$ and $y = 0.3195$).

2.6.3. pH

The pH was determined using 1 g of the flours or beverage formulation to 5 mL of distilled water.

2.7. Volatile content analysis

2.7.1. Extraction and chemical identification

The formulations (CTRLBev, FJSBev, and DJSBev) (3 g) were placed in a 20 mL SPME vial with 5 μL of 1,2-dichlorobenzene in methanol (130.6 μg/mL) and vortexed for 2 min. After equilibrium at 45 °C for 15 min, triple-phase fiber (50/30 μm DVB/CAR/PDMS from Supelco®) was placed 2 cm above the sample for 55 min under magnetic agitation (60 rpm). The volatile compounds extracted by the fiber were analyzed by GC–MS in an Agilent 5975C Inert XL Turbo Pump GC/MS equipped with a Supelcowax® 10 carbowax column (20 m, 0.25 mm i.d., 0.25 μm film thickness). Splitless injection (200 °C) was used for 1 min to desorb the volatile compounds. The oven was maintained at 40 °C for an additional 8 min. The temperature was raised at 4 °C/min to 200 °C and then at 10 °C/min to 280 °C, totaling 56 min. The MS analysis was carried out in scan mode at 70 eV, with m/z values within the range of 40 to 500. Helium was used as a carrier gas at a flow rate of 1 mL/min under constant flow. Each sample was analyzed in triplicate.

2.7.2. Evaluation parameters

Linear retention indices (LRIs) were obtained using a series of n-alkane standards (C7−C30). LRIs and mass spectra were compared against the authentic sample or Nist 11th library (> 80% similarity),

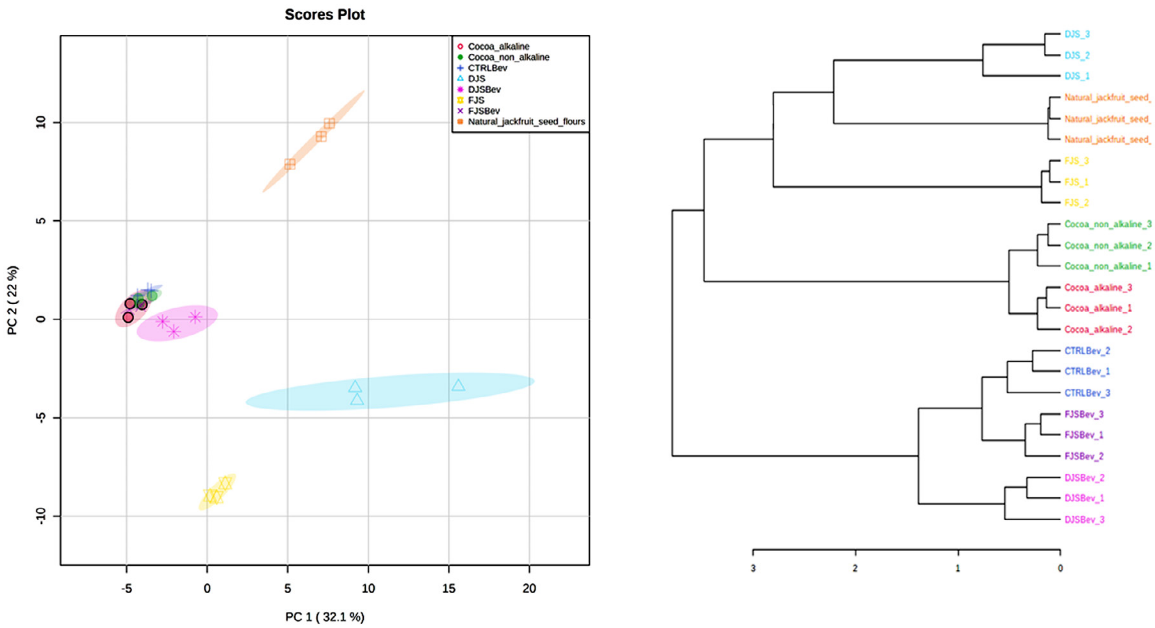

Fig. 1. A. Principal components analysis (PCA) of all volatile constituents (GC/MS) identified in jackfruit seed flours, cocoa powder, and control/experimental beverages. B. GC/MS dendrogram data (Pearson Average) of jackfruit seed flours, cocoa powder, and control/experimental beverage formulations.

Nist Chemistry Webbook, and online LRI and Odour databases. Threshold values were obtained from The Odour and Flavour (OFTV) platform. The approximate relative concentration of each compound was obtained by comparing the peak area of the compound against that of the internal standard (1,2- dichlorobenzene) using 1 as a response factor.

2.8. Statistical analysis

The data were analyzed in Metaboanalyst v. 4.0. The volatile areas were normalized by a reference feature (internal standard - 1,2-dichlorobenzene) and auto-scaling (mean-centered and divided by the standard deviation of each variable). Principal Components Analysis (PCA) was carried out using the prcomp package. The calculation was based on singular value decomposition. 2D score plots and a biplot were computed from selected PCs. Hierarchical clustering was carried out using the hclust package. Clustering results were expressed as dendrograms and a heatmap indicating Pearson distance measures and Average's clustering algorithm. Volatile content data were submitted to a two-way analysis of variance (ANOVA) followed by Tukey's posthoc test and Fisher's least significant difference (LSD). Statistical tests were carried out in XLStat, considering a 5% significance level.

3. Results

The three key results of this study were that (i) FJSBev was similar to the non-alkaline cocoa powder beverage (CTRLBev); (ii) similar volatile groups were identified in these samples (acids, alcohols, aldehydes, ester, furans, and pyrazines); (iii) the beverages contained volatile compounds with a low threshold of cocoa attributes (butter, cocoa, coffee, floral, fruit, green, honey, mushroom, nut, and roasted).

The moisture content between the beverages was not statistically different ($p > 0.05$). However, significant differences in luminosity and chroma parameters were observed ($p < 0.05$), but the chroma measurements of FJSBev were not different from those of non-alkaline cocoa powder ($p > 0.05$). CTRLBev and FJSBev had a similar pH ($p > 0.05$) (Supplementary Table).

Volatile concentrations were plotted from selected PCs, and the cluster analysis data were represented in a biplot graph based on the area of the compounds (Fig. 1A and B). Two PCs explained 56% of the variance. Five groups were tested in the cluster analysis (natural jackfruit seed flours; dry jackfruit seed flours; fermented jackfruit seed flours; DJS-Bev; and CTRLBev, FJSBev, alkaline cocoa powder, non-alkaline cocoa powder). Most similarities were observed between cocoa powders and fermented beverages. At a cutoff of 1.0, the Pearson Average (Fig. 1B) indicated that alkaline and non-alkaline cocoa had similar volatile content as well as CTRLBev and FJSBev.

As shown in Fig. 2, PCA data indicated a significant difference in the volatile content between DJSBev and the other beverages. CTRL-Bev and FJSBev showed a similar volatile profile associated with the following acids, alcohols and esters (Table 2): propanoic acid, 2 methyl (prp3), 2,3-butanediol (but3), pentyl/ciclopropene (nd1), ethyl phenylacetate (phe2), 2-phenylethyl alcohol (phe3), 1-(1H-pyrrol-2yl)-ethanone (one6), acetic acid (ace1), and pentanoic acid (pen3). Propanoic acid is associated with butter and sweet aromas; 2 methyl (prp3) has a threshold value of 0.013 mg m^{-3} (low); 2,3-butanediol (but3) and 2-phenylethyl alcohol (phe3) are included in the cocoa category and reported to have floral, honey, and rose aromas; in addition, 2,3-butanediol (but3) is reported to have cocoa, coffee, and cupuaçu aroma. Both but3 and phe3 produce a pleasant combination of aromas. Acetic acid (ace1) and pentanoic acid (b3) have 0.017 and 0.001 mg m^{-3} threshold values; acid, vinegar, fruity, and cheese are aroma descriptors for acetic acid (ace1) and pentanoic acid (pen3).

Table 2 shows the tentative identification and quantification of volatile compounds in the samples. The findings showed no significant difference in the volatile content of CTRLBev and FJSBev ($p > 0.05$). The following compounds were tentatively identified: furan, 2-pentyl (a6), ethyl n-octanoate (oct3), 1-Octen-3-ol (oct4), alfa-copaene (alf1), benzaldehyde (ben1), propanoic acid, 2-methyl (prp3), 2-methyl-6-(3-methylbutyl) pyrazine (pyr18), butanoic acid, 3 (2)-methyl (but5), Benzyl alcohol (ben2), 2-phenylethanol (phe3), 2-ethylhexanal (hex4), acetic acid (ace1), E-Cinnamaldehyde (e1), levomenthol (lm), pyrazine (p1), pyrazine, methyl (p2), pyrazine, ethyl (pyr5), pyrazine, 2-ethyl-6 (5)-methyl (pyr7), pyrazine, 2,6-dimethyl (pyr4), dimethyl ether (edi1), (E,E)−2,4-heptadienal (hep1), pyrazine, 2,5-dimethyl (pyr3), and (E,Z)−3,5-octadien-2-one (oct5). These compounds are acids, al-

Table 2
Approximate relative quantification (μg/100 g flour) and identification compounds in jackfruit seed flours, alkaline cocoa, not-alkaline cocoa powder and beverages formulated with these ingredients.

						Flours					Beverages					
ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	DJS	FJS	Alkaline cocoa	Non-alkaline cocoa	P-value	CTRLBev	FJSBev	DJSBev	P-value	Threshold (mg/m^3)	Reference
eac1	889	889	93	Ethyl Acetate	balsamic, contact glue, grape, pineapple, and sweet	33 ± 12.9	27 ± 9.9	nd	nd	***	nd	nd	nd		1.03	Komthong et al., 2006
one1	906	908	93	2-Butanone		nd	nd	nd	nd		5 ± 0.7a	12 ± 5.2b	5 ± 2.6ab	*		
pdi1	915	nd	66	Propanal, 2,2-dimethyl-	caramel, cocoa, green, malt, and nut	nd	nd	17 ± 7.2	nd		nd	nd	nd		0.14	Hellman & Small, 1974
edi1	938	938	88	Dimethyl ether	potato and vinegar	65 ± 33.5	26 ± 3.8	nd	11 ± 6.6	***	28 ± 19.3	13 ± 10.1	22 ± 11.9	ns		
pen1	977	978	91	Pentanal	almond, green, malt, oil, and pungent	13 ± 10.1	nd	nd	nd	***	nd	nd	nd		0.85	Cometto-Muñiz & Abraham, 2010
hep1	1012	1012	88	(E,E)−2,4-heptadienal		8 ± 4.7	12 ± 4.4	nd	nd	***	22 ± 4	35 ± 9.7	33 ± 7	ns		
hex1	1050	nf	97	Hexane, 3,3-dimethyl-	coffee and cheese	nd	nd	24 ± 12.5	nd	***	nd	nd	nd			
hex2	1080	1084	91	Hexanal		439 ± 146.7	32 ± 7.8	61 ± 33.8	nd	***	28 ± 9.6a	27 ± 7a	151 ± 40.8b	**		
oct1	1138	nf	93	Octane, 4-ethyl-	alkane, fat, oil, and sweet	22 ± 4.8	12 ± 1.3	nd	nd	****	nd	nd	nd		550	Jones, 1955
dio1	1154	nf	89	1,3-Dioxolane, 2,2,4-trimethyl / Ethyl 2,4-dimethyl-1,3-dioxolylacetate 2		47 ± 18.8	17 ± 4.2	nd	nd	***	nd	nd	nd			
hep2	1172	1190	73	2-Heptanone or Heptanal	citrus, dry fish, fat, green, and nut	24 ± 5.8	18 ± 3.9	nd	nd	****	nd	nd	nd		0.26	Cometto-Muñiz & Abraham, 2010
hex3	1175	1177	85	Hexanoic acid, methyl ester		nd	nd	nd	nd	****	nd	nd	nd			
but1	1182	1190	86	2-Butenal, 2-methyl-/ 2-methyl-1-butanol	apple, fruit, grass, green, and solvent	18 ± 1.2	nd	nd	nd	****	nd	nd	nd			
euc1	1190	nf	80	Eucalyptol = 1,8-oxido-p-menthane	camphor, cool, eucalyptol, mint, and sweet	13 ± 4.2	13 ± 3.3	nd	nd	****	nd	nd	nd		0.0031	Güntert et al., 2001
pyr1	1193	1194	80	Pyrazine		nd	nd	nd	nd		3 ± 1.1	3 ± 0.6	4 ± 0.8	ns		
fur1	1211	1210	88	Furan, 2-hexyl- / Furan, 2-pentyl	butter, floral, fruit, and green bean	74 ± 8.9	37 ± 2.5	nd	nd	****	7 ± 2.6a	14 ± 0.6a	28 ± 8.9b	***	0.019	Dong et al., 2008
hex4	1216	1216	92	Hexanoic acid, ethyl ester / 2-Ethylhexanal	acid, cheese, goat, pungent, and rancid	6 ± 1.9	10 ± 1.4	nd	nd	****	7 ± 2	7 ± 1.8	13 ± 6.4	ns	0.0014–0.010	Güntert et al., 2001
phe1	1231	nf	92	Phenol, 3,5-dimethyl-	phenol and smoke	33 ± 11.5	35 ± 10.8	nd	nd	****	nd	7 ± 2.8	nd		0.003	Stuver 1958
pen2	1234	1231	91	1-Pentanol	balsamic, fruit, green, medicine and yeast	30 ± 12.8	nd	nd	nd	****	nd	nd	nd		1.1	Janicek, G.; Pliska, V.; Kubatova, 1960
hep3	1250	nf	91	Heptane, 2,2,4,6,6-pentamethyl	bell pepper, blue cheese, cinnamon, green and nut	4 ± 1.5	nd	nd	nd	****	nd	nd	nd		0.023	Cometto-Muñiz & Abraham, 2010
pyr2	1253	1255	93	Pyrazine, methyl-	cocoa, green, hazelnut, popcorn and roasted	47±11.2	15±1.4	40±16.6	26±11.3	***	16±1.8a	17±2.4a	44±3.8b	****	1.9	Fors & Olofsson, 1985

(*continued on next page*)

Table 2 (*continued*)

ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	Flours DJS	FJS	Alkaline cocoa	Non-alkaline cocoa	P-value	Beverages CTRLBev	FJSBev	DJSBev	P-value	Threshold (mg/m^3)	Reference
cyc1	1269	nf	94	Cyclohexane, hexyl-	milk products	10±4.1	nd	nd	nd	****	nd	nd	nd			
prp1	1273	1265	91	2-Propanone, 1-methoxy-	*Artocarpus sp*	4 ± 1.4	4 ± 0.2	nd	nd	****	3 ± 0.5	nd	4 ± 1.1			
hex5	1283	nf	92	Hexyl octyl ether		nd	21±3.4	nd	nd	****	nd	nd	nd			
pyr3	1316	1316	90	Pyrazine, 2,5-dimethyl-	burnt plastic, cocoa, medicine, roast beef, roast nut/fat, green, mushroom, and soap	31±2.8	18±1.2	17±7.2	12±3.7	***	6 ± 0.3a	10±1.8a	25±3.2b	****	1.82 /0.056	Grosch et al., 1996
pyr4	1323	1324	90	Pyrazine, 2,6-dimethyl-	cocoa, coffee, green, roastbeef, and roasted nut	14±1.9	7 ± 0.2	nd	nd	****	2 ± 0.1a	4 ± 0.5a	10±1.5b	***	0.25	Fors & Olofsson, 1985
pyr5	1325	1325	90	Pyrazine, ethyl-	green, iron scorch, must, peanut butter, and roasted	37 ± 6.2	31±3.3	nd	nd	****	9 ± 0.9a	14±0.2a	31±6.9b	***	0.25	Grosch et al., 1996
one2	1329	1320	93	5-Hepten-2-one, 6-methyl-		nd	nd	nd	nd	****	nd	nd	nd			
pry6	1341	1338	94	Pyrazine, 2,3-dimethyl-	caramel, cocoa, hazelnut, peanut butter, and roasted	9 ± 0.9	9 ± 0.5	nd	nd	****	2 ± 0.1a	4 ± 0.4b	6 ± 0.5c	****	0.9	Fors & Olofsson, 1985
hex6	1348	1348	93	1-Hexanol	flower, fruit, green, herb, and wood	8 ± 3.2	nd	nd	nd	****	nd	nd	nd		9.94	Carlin et al. 1986
iso1	1350	1350	92	2-Isopropyl-5-methylhex-2-enal /2-isopropyl-4-methylthiazole	cocoa category	13±5.6	41±1.4	nd	nd	****	nd	nd	nd			
art1	1354	1359	92	Artemiseole or 2-n-Propyl-4-ethyl-5-methyloxazole	pyrans	nd	10±1.1	nd	nd	****	nd	nd	nd			
one3	1491	nf	74	3-Nonen-2-one	deep fried, fat, geranium, green, and metal	5 ± 2	nd	nd	nd		nd	nd	nd		0.0002	Dong et al., 2008
tri1	1373	1367	80	Dimethyl trisulfide/ trimethylthiazole 127 massa	cabbage, fish, onion, sulfur, and sweat	nd	3 ± 0.2	nd	nd	****	nd	nd	nd		0.014	Counet et al., 2002
pyr7	1380	1381	59	Pyrazine, 2-ethyl-6 (5)-methyl-	green, nut, and roasted	24±3.9	14±0.4	nd	nd	****	4 ± 0.4a	8 ± 1.5a	16±2.4b	***		
non1	1385	1384	93	Nonanal		10±4.1	nd	nd	nd	***	8 ± 2.6a	9 ± 2ab	12±1.3b	*		
pyr8	1386	1387	95	Pyrazine, 2-ethyl-5 (6)-methyl	fruit, green, nut, roast, and sweet	20±2.8	14±0.6	7 ± 2.8	nd	****	2 ± 0.4a	6 ± 1.1b	14±1.7c	****	0.036	Fors & Olofsson, 1985
one4	1399	1399	95	3-Octen-2-one /1-octen-3-one		60±14.6	nd	nd	nd	****	nd	nd	nd			
pyr9	1400	1400	96	Pyrazine, trimethyl-	cocoa, earth, must, potato, and roast	32±9.6	49±3.2	18±7.9	12±4	****	7 ± 0.2a	15±0.8b	22±2.7c	***	0.05–0.096	Grosch et al., 1996
hex7	1408	nf	92	1,3-Hexadiene, 3-ethyl-2-methyl	nut, and found in rice	9 ± 3.5	nd	nd	nd	****	nd	nd	3 ± 1.8			
oct2	1433	1430	93	2-Octenal, (E)-	fat, fishi, oil, green, nut, and sweet	58±16.5	nd	nd	nd	****	nd	nd	nd		0.014	Eriksson et al., 1976
oct3	1422	1423	93	Octanoic acid, ethyl ester /Ethyl n-octanoate	acid, cheese, fat, rancid, and sweat	nd	nd	nd	nd	****	2 ± 0.2	2 ± 0.3	2 ± 0.5	ns	0.011–0.018	Pino & Mesa, 2006

(*continued on next page*)

Table 2 (*continued*)

ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	Flours DJS	FJS	Alkaline cocoa	Non-alkaline cocoa	P-value	Beverages CTRLBev	FJSBev	DJSBev	P-value	Threshold (mg/m^3)	Reference
pyr10	1426	1429	93	Pyrazine, 2,6-diethyl-		19±8.2	nd	nd	nd		nd	nd	6 ± 0.4			
ace1	1433	1435	100	Acetic acid	acid, fruit, pungent, sour, and vinegar	6 ± 0.4	284±12.3	627±227.5	960±252.1	****	107±2.9ab	130±27.3b	94±10.3a	*	0.017–0.020	Pino & Mesa, 2006
oct4	1438	1427	100	1-Octen-3-ol	black currants	37±4.3	nd	nd	nd	****	3 ± 0.3	4 ± 0.9	16±13.4	ns		
pyr11	1437	1443	100	Pyrazine, 3-ethyl-2,5-dimethyl-	cocoa, roast, rum, smoke, and cocoa category	47±25.3	26±5.8	nd	nd	***	nd	nd	nd			
pyr12	1444	1444	100	2,5-Diethylpyrazine	cereal, earth, hazelnu, and meat	8 ± 3.3	nd	nd	nd		nd	nd	nd		0.050	Fors & Olofsson, 1985
fur2	1447	1449	80	3-Furaldehyde		nd	nd	nd	nd		3 ± 0.8a	3 ± 1.1a	nd	****		
men1	1470	1478	76	l-Menthone ou Cyclohexanone, 5-methyl-2-(1-methylethyl)-		nd	nd	nd	nd	****	nd	nd	nd			
pyr13	1451	1454	94	2,3-Dimethyl-5-ethylpyrazine	burnt, earth, green bean, and popcorn	26±10.3	40±5.6	nd	nd	****	4 ± 1.6,0a	11±2.4b	13±2.6b	***	0.2	Grosch et al., 1996
vin1	1453	nf	95	Ether, 6-methylheptyl vinyl		26±30	nd	nd	nd		nd	nd	nd			
pyr14	1463	1467	95	Pyrazine, tetramethyl-	cocoa, coffe, green, mocha, and roast	10±3.8	71±8	13±8	13±6.4	****	5 ± 0.3a	12±1.3b	9 ± 2.7ab	***	>2	Grosch et al., 1996
alf1	1471	nf	100	Alfa-copaene		nd	nd	nd	nd		16±3.2	34±9.3	26±11.8	ns		
hex8	1472	1480	90	1-Hexanol, 2-ethyl-		nd	nd	nd	nd		nd	nd	nd			
cyc2	1475	nf	85	Cyclohexene, 1-ethyl-		nd	nd	nd	nd		nd	nd	nd			
pyr15	1501	1501	89	Pyrazine, 3,5-diethyl-2-methyl-	earth, meat, potato, and roast	12±6.7	9 ± 0.7	nd	nd	***	1 ± 0.3a	3 ± 0.1b	4 ± 0.5b	***	0.000014	Grosch et al., 1996
prp2	1483	1483	90	2-propyl-3-methylpyrazine		12±4.8	nd	nd	nd		nd	nd	nd			
eth1	1484	1485	89	Ethanone, 1-(2-furanyl) ou 2-acetylfuran	bread, cocoa, hazelnut, licorice, and wainut	2 ± 0.7	nd	nd	nd		nd	nd	2 ± 0.2		>2	Schieberle & Hofmann, 1997
pyr16	1496	1503	96	2,3,5-Trimethyl-6-ethylpyrazine	cocoa and coffee category	13±5	19±2.5	nd	nd	****	nd	3 ± 0.5	2 ± 0.4			
oct5	1497	1500	96	Octadien-2-one / 3,5-Octadien-2-one/(E,Z)–3,5-octadien-2-one	fat, fruit, and mushroom	13±2.9	nd	nd	nd	****	2 ± 0.3	6 ± 3.3	16±15.7	ns		
ben1	1501	1502	99	Benzaldehyde	bitter, almond, burnt sugar, cherry, malt, and roasted pepper	10±1.9	9 ± 0.6	29±12.8	27±8.5	***	14±1.6a	18±3.5a	23±2.0b	*	13	Janicek, G.; Pliska, V.; Kubatova, 1960
pyr17	1507	1507	100	Pyrazine, 2,5-dimethyl-3-(2-methylpropyl)-		7 ± 2.9	3 ± 0.4	nd	nd	***	nd	nd	1 ± 1.1			
fur3	1517	1525	88	Furan, 2-butyltetrahydro- ou 1-(2-Furanyl)–2-propanon		16±6.4	nd	nd	nd	****	nd	nd	nd			
but2	1522	nf	95	2,3-Butanediol, [S-(R*,R*)]-	cream, floral, fruit, herb, and rubber	nd	18±0.6	45±11.2	40±12.3	****	17±2.9b	12±1.7ab	9 ± 1.3a	***		
cyc3	1539	nf	97	Cyclopropane, pentyl		nd	nd	nd	nd		nd	nd	2 ± 0.7			
fur4	1540	1545	82	Furan, 2-butyltetrahydro- / 2-propionylfuran		nd	nd	nd	nd	****	nd	nd	nd			
ace2	1545	nf	80	Ethyl Acetate	balsamic, contact glue, grape, pineapple, and sweet	nd	6 ± 0.4	16±4.7	12±4.4	****	6 ± 0.6b	4 ± 0.4a	3 ± 0.2a	***	1,12	Janicek, G.; Pliska, V.; Kubatova, 1960

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Table 2 (*continued*)

ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	Flours: DJS	FJS	Alkaline cocoa	Non-alkaline cocoa	P-value	Beverages: CTRLBev	FJSBev	DJSBev	P-value	Threshold (mg/m³)	Reference
prp3	1551	1560	91	Propanoic acid, 2-methyl-	burnt, butter, cheese, and rancid, sweat	nd	8 ± 0.5	17±6.5	14±4.1	***	3 ± 0.2	4 ± 1	3 ± 0.5	ns	0.013	Ueno et al., 2009
oct6	1554	1562	92	3,5-Octadien-2-one	fat, fruit, and mushroom	8 ± 3.1	nd	nd	nd	****	nd	nd	nd			
one5	1559	1558	93	Acetoin = -3-Hydroxy-2-butanone	butter, cream, green pepper, rancid, and sweat	nd	4 ± 0.4	12±3.5	8 ± 2.7	****	4 ± 0.4b	3 ± 0.2a	3 ± 0.4a	***	0.259	Fan et al., 2015
but3	1562	1568	81	2,3-Butanediol, [S-(R*,R*)]-	cocoa category, coffee, and cupuacu	nd	13±0.6	33±8.7	28±8.7	****	13±1.8b	9 ± 1.1a	7 ± 1.2a	***		
nd1	1570	nf		ni		nd	nd	nd	nd		3 ± 0.4a	6 ± 1.1b	7 ± 0.9b	***		
eth2	1579	1575	97	Ethanone, 1-(2-methyl-1-cyclopenten-1-yl)- / 2-propionylfuran		8 ± 1.6	12±1.1	nd	nd	****	1 ± 0.2a	3 ± 0.4b	4 ± 0.2c	****		
fur5	1596	1591	97	2(5H)-Furanone, 5,5-dimethyl- / 3-Methyltetrahydro-2-furanon		25±3.6	13±1.7	nd	nd	****	nd	3 ± 1.1	13±1.4			
fur6	1606	1606	98	2-Acetyl-5-methylfuran	nut, roasted, and vegetable	3 ± 0.6	nd	nd	nd	****	nd	nd	nd			Fan et al., 2015
pyr18	1615	nf	86	2-Isoamyl-6-methylpyrazine = 2-methyl-6-(3-methylbutyl) pyrazine	cocoa category	9 ± 1.2	10±1.1	36±13	35±12.7	***	6 ± 0.2	8 ± 2.9	8 ± 0.4	ns		
pyr19	1616	1616	89	5H-5-Methyl-6,7-dihydrocyclopentapyrazine		8 ± 5.2	4 ± 0.5	nd	nd	***	nd	nd	nd			
but4	1624	1626	99	Butanoic acid, 4-hydroxy-		3 ± 1.1	nd	nd	nd		7 ± 0.1b	5 ± 0.3a	8 ± 1.2b	***		
pyr20	1629	nf	84	2,5-Dimethyl-3-(2-methylbutyl)pyrazine / 2-Butyl-3-methylpyrazine	brown, nut, and sweet	11±6	nd	nd	nd	***	nd	nd	nd			
lev1	1636	1612	94	Levomenthol		nd	nd	nd	nd	****	6 ± 1.4	11±3	10±5.5	ns		
eth3	1642	nf	94	3-Ethyl-4-nonanol		nd	nd	nd	nd	****	nd	nd	nd			
ace3	1648	1652	86	Acetophenone		nd	nd	nd	nd		4 ± 0.9a	6 ± 1.0a	8 ± 1.2b	*		
pyr21	1657	1657	91	2-(3-Methylbutyl)–3,5-dimethylpyrazine (174)	cocoa category	6 ± 3	10±3.3	nd	nd	***	nd	nd	nd			
fur7	1657	1662	78	2-Furanmethanol	burnt, caramel, cooked, solvent, and wood	nd	18±6.1	nd	nd	****	nd	nd	nd			
fur8	1658	1663	93	Pentanoic acid, 2-methyl-, anhydride / (2-Furyl)-(5-methyl-2-furyl)methan		11±4.2	nd	nd	nd	****	nd	nd	nd			
but5	1666	1669	93	Butanoic acid, 3 (2)-methyl-	apple, banana, cheese, ester, and floral	7 ± 1	40±3.7	97±33.9	76±24.3	***	20±1.1	19±6.1	17±3.3	ns		
prp4	1669	nf	90	Propanoic acid	fat, pungent, rancid silage, and soy	nd	4 ± 0.4	6 ± 2	nd	****	nd	nd	nd		0.08	Hellman & Small, 1974

(*continued on next page*)

Table 2 (*continued*)

ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	Flours DJS	FJS	Alkaline cocoa	Non-alkaline cocoa	P-value	Beverages CTRLBev	FJSBev	DJSBev	P-value	Threshold (mg/m^3)	Reference
fur9	1671	1671	89	2(3H)-Furanone, 5-ethenyldihydro-5-methyl- / dihydro-5-isopropyl-3(2H)-furanone		12±4.7	nd	nd	nd	***	nd	nd	nd			
pyr22	1682	1681	89	1H-Pyrazole, 3-methyl/3(2),5-Dimethyldihydrocyclopentapyrazine	tequila	22±11.3	56±15.8	nd	nd	****	nd	9 ± 2.2	22±18			
pyr23	1683	1683	86	5H–Cyclopentapyrazine, 6,7-dihydro-2,5-dimethyl	cocoa category and coffee	6 ± 2.5	nd	nd	nd		nd	nd	nd			
pyr24	1702	1709	76	2,3-Dimethyl-5-isopentylpyrazine / 2-Methyldihydrocyclopentapyrazine	cocoa category	nd	11±2.3	nd	nd	****	nd	nd	nd			
non2	1703	1705	81	2,4-Nonadienal, (E,E)-		nd	nd	nd	nd	****	nd	nd	nd			
nd2	1718	1719	89	2-murirolene		nd	nd	nd	nd		2 ± 0.3a	4 ± 1.2b	4 ± 0.7b	*		
pyr25	1718	1709	89	2,3,5-Trimethyl-6-isopentylpyrazine / Ethyltrimethyl or Diethylmethylpyrrole	cocoa category	nd	5 ± 1	nd	nd	****	nd	nd	nd			
prp5	1728	1729	89	Ethyl Acetate ??? 1,2-Propanediol, 2-acetate? / n-Decyl n-propionate		nd	5 ± 0.5	nd	nd	****	nd	3 ± 0.2	nd			
phe2	1775	1770	70	Acetic acid, 2-phenylethyl ester / ethyl phenylacetate		nd	nd	nd	nd		4 ± 0.9a	5 ± 0.9ab	6 ± 1.4b	*		
pen3	1793	1791	97	Pentanoic acid	cheese, fecal, putrid fruit, rancid, and sweat	20±12.7	6 ± 0.5	nd	nd	***	6 ± 1.2a	11±1.5a	21±5.2b	***	0.001	Blank & Schieberle, 1993
ben2	1854	1856	94	Benzyl alcohol		nd	nd	nd	nd		2 ± 0.7	3 ± 0.5	3 ± 0.7	ns		
sul1	1903	nf	97	Dimethyl sulfone		nd	nd	nd	nd		2 ± 0.2	2 ± 1	nd			
phe3	1918	1923	100	Phenylethyl Alcohol / 2-phenylethanol	floral, honey, and rose	nd	7 ± 2.3	27±12.8	17±7.3	***	10±1b	9 ± 0.9ab	7 ± 1.7a	*		
one6	1973	1980	96	1-(1H-pyrrol-2yl)ethanone		nd	nd	nd	nd		2 ± 0.5a	3 ± 0.4b	4 ± 1.0b	*		
pyr26	2031	2026	91	1H-pyrrole-2-carboxaldehyde / 5-Methyl-5H-cyclopentapyrazine		nd	nd	nd	nd		nd	nd	3 ± 0.4			
cin1	2046	2045	92	Cinnamaldehyde, (E)-	*Artocarpus sp*, cheeses, and beer	9 ± 2.4	11±3.8	nd	nd	**	103±28.5	152±20.5	126±33.6	ns	0.00003	Appell, 1969

(*continued on next page*)

Table 2 (*continued*)

ID	LRI expt	LRI wax20	NIST (%)	Compound name	Aromas	Flours: DJS	Flours: FJS	Flours: Alkaline cocoa	Flours: Non-alkaline cocoa	Flours: P-value	Beverages: CTRLBev	Beverages: FJSBev	Beverages: DJSBev	Beverages: P-value	Threshold (mg/m^3)	Reference
pyo1	2050	2053	99	2-Pyrrolidinone / 2-Acetyl-5-methylpyrrole		Nd	nd	nd	nd		nd	2 ± 0.6	3 ± 0.4			
gly1	2073	nf	69	Glycerol 1,2 diacetate		Nd	nd	nd	nd		1 ± 0.2	2 ± 0.3	2 ± 1.1	ns		

ID – Identifier; LRI expt – Linear retention index on Supelcowax 10 carbowax column (20 m, 0.25 mm i.d., 0.25 μm film thickness), calculated from a linear equation between each pair of straight chain alkanes C6–C30.; LRI wax 20 – LRI to data comparation; NIST (%) – percentual of similarity in comparison NIST 11.1 library; DJS – dry jackfruit seeds; FJS – fermented jackfruit seeds; CTRLBev – non-alkaline cocoa powder beverage; FJSBev – fermented jackfruit seed flour beverage; DJSBev – dry jackfruit seed flour beverage; nf – not found; ni – not identified; nd – not detected; ns – no significant difference between means (p>0.05); * significant at the 5% level; ** significant at the 1% level; ***significant at the 0.1% level; ****significant at the 0.01% level; For beverages each row, cells containing the same letter are not significantly different from each other at p<0.05.

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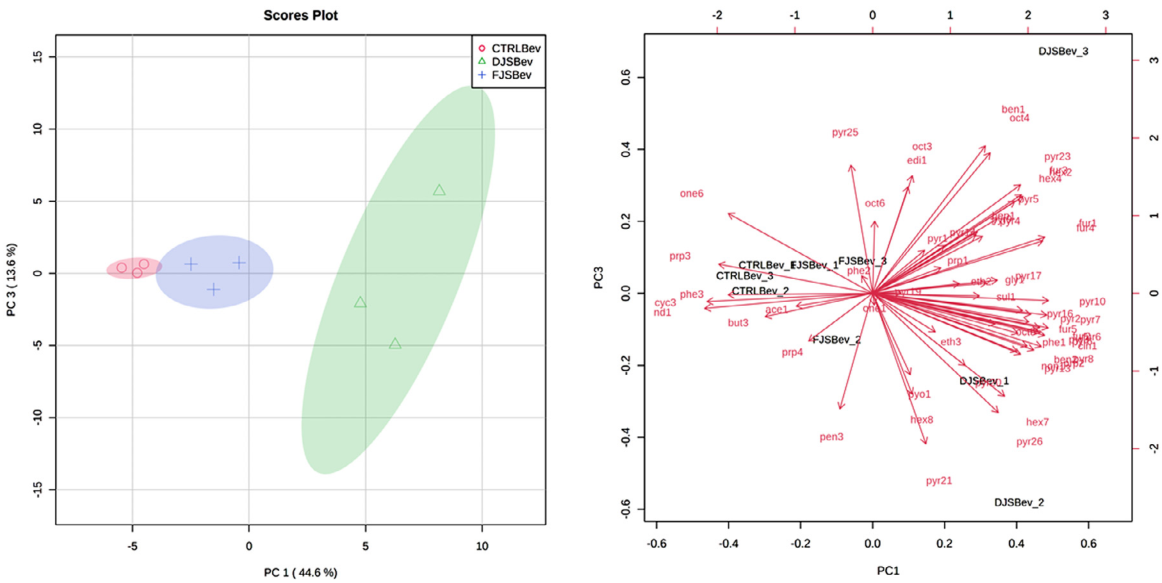

Fig. 2. A. Principal components analysis (PCA) of all volatile constituents (GC/MS) detected in the control beverage containing non-alkaline cocoa powder (CTRLBev), and dry jackfruit seed flour beverage (DJSBev) and fermented jackfruit seed flour beverage (FJSBev). B. Principal components analysis (PCA) of the projection of all volatile constituents (GC/MS) contained in the beverage formulations.

cohols, aldehydes, esters, and pyrazines. Butter, green, and floral are aromas attributed to furan, 2-pentyl (fur1), and 3-(2)-methyl a34; benzaldehyde (ben1) produces an almond aroma; and E-Cinnamaldehyde (cin1) has aromas associated with *Artocarpus* species. A typical cocoa aroma was described for 2-methyl-6-(3-methylbutyl) pyrazine (pyr18); pyrazine, methyl (pyr2); pyrazine, ethyl (pyr5); pyrazine, 2-ethyl-6 (5)-methyl (pyr7); pyrazine, 2,6-dimethyl (pyr4); pyrazine, 2,5-dimethyl (pyr3); and (E,Z)−3,5-octadien-2-one (oct5) (Frauendorfer and Schieberle, 2008). These compounds also produce the roasted, nut, coffee, and mushroom aromas with a low threshold value (Table 2) and are present in cocoa and coffee, which suggests that FJS flours can partially or totally replace cocoa powder.

Pearson Average distribution at a score cutoff of 2.0 and heat maps of volatile contents (Fig. 3A and B) showed two groups of beverages, namely: dry beverage, and control and fermented beverages. The compounds detected both in CTRLBev and FJSBev were: hexanal (hex2); furan, 2-pentyl (fur1); nonanal (non1); 1-octen-3-ol (oct4); 3-furaldehyde (fur2); benzaldehyde (ben1); 3-methyltetrahydro-2-furanon (fur5); benzyl alcohol (ben2); 2-acetyl-5-methylfuran (fur6); 2-ethylhexanal (hex4); 2,5-dimethyl-6,7-dihydro-(5H)-cyclopentapyrazine (pyr23); E-cinnamaldehyde (cin1); 1-(2-furanyl)−2-propanon (fur3); 2-propionylfuran (fur4); pyrazine, methyl (pyr2); pyrazine, ethyl (pyr5); pyrazine, 2-ethyl-6 (5)-methyl (pyr7); pyrazine, 2,6-diethyl(pyr10); 2,3,5-trimethyl-6-ethylpyrazine (pyr16); pyrazine, 2,6-dimethyl (pyr4); pyrazine, 2,5-dimethyl (pyr3); pyrazine, 2-ethyl-5 (6)-methyl (pyr8); and 1,3-Hexadiene, 3-ethyl-2-methyl (hex7). These compounds are alcohols, aldehydes, furans, and pyrazines. Cocoa, nut, coffee, green, roasted, sweet and fruit are aroma attributes of 2-acetyl-5-methylfuran (fur6); pyrazine, methyl (pyr2); pyrazine, ethyl (pyr5); pyrazine, 2-ethyl-6 (5)-methyl (pyr7); pyrazine, 2,6-diethyl (pyr10); 2,3,5-trimethyl-6-ethylpyrazine (pyr16); pyrazine, 2,6-dimethyl (pyr4); pyrazine 2-ethyl-5 (6)-methyl (pyr8); and 1,3-Hexadiene and 3-ethyl-2-methyl (hex7). These compounds have low threshold values, particularly pyrazine 2-ethyl-5 (6)-methyl (pyr8) (0.036 mg m-3). These data highlight the similarities between cocoa powder and FJS flours and open possibilities to improve jackfruit seed application in food formulations.

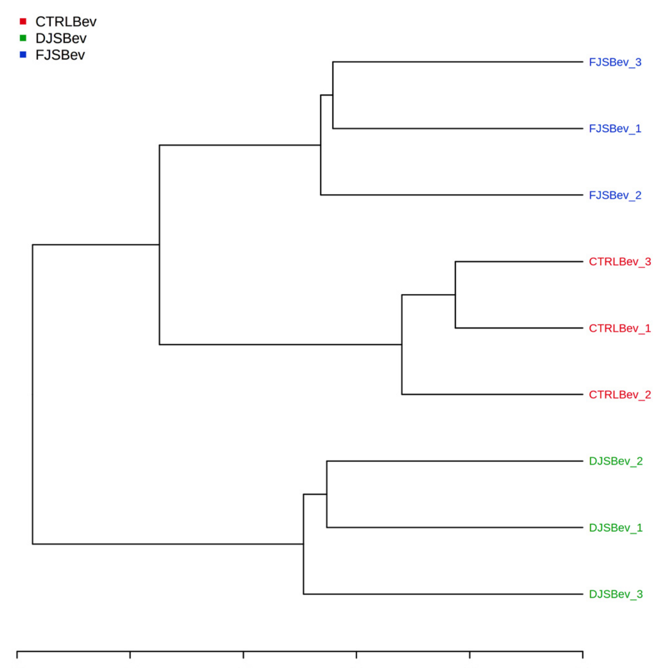

Fig. 3. GC/MS dendrogram data (Pearson Average) of the volatile constituents identified in the control beverage containing non-alkaline cocoa powder (CTRLBev), and dry jackfruit seed flour beverage (DJSBev) and fermented jackfruit seed flour beverage (FJSBev).

Fig. 4 shows that alkaline and non-alkaline cocoa and FJS flours are in the same area of the PCA. Similar volatile compounds included ethyl acetate (ace2), propanoic acid, 2-methyl (prp3), 3-hydroxy-2-butanone (one5), 2-phenylethanol (phe3), acetic acid (ace1), and propanoic acid (prp4). Propanoic acid, 2-methyl (prp3), 3-Hydroxy-2-butanone (one5), 2-phenylethanol (phe3), and acetic acid (ace1) are critical constituents determining the cocoa quality Fig. 5.

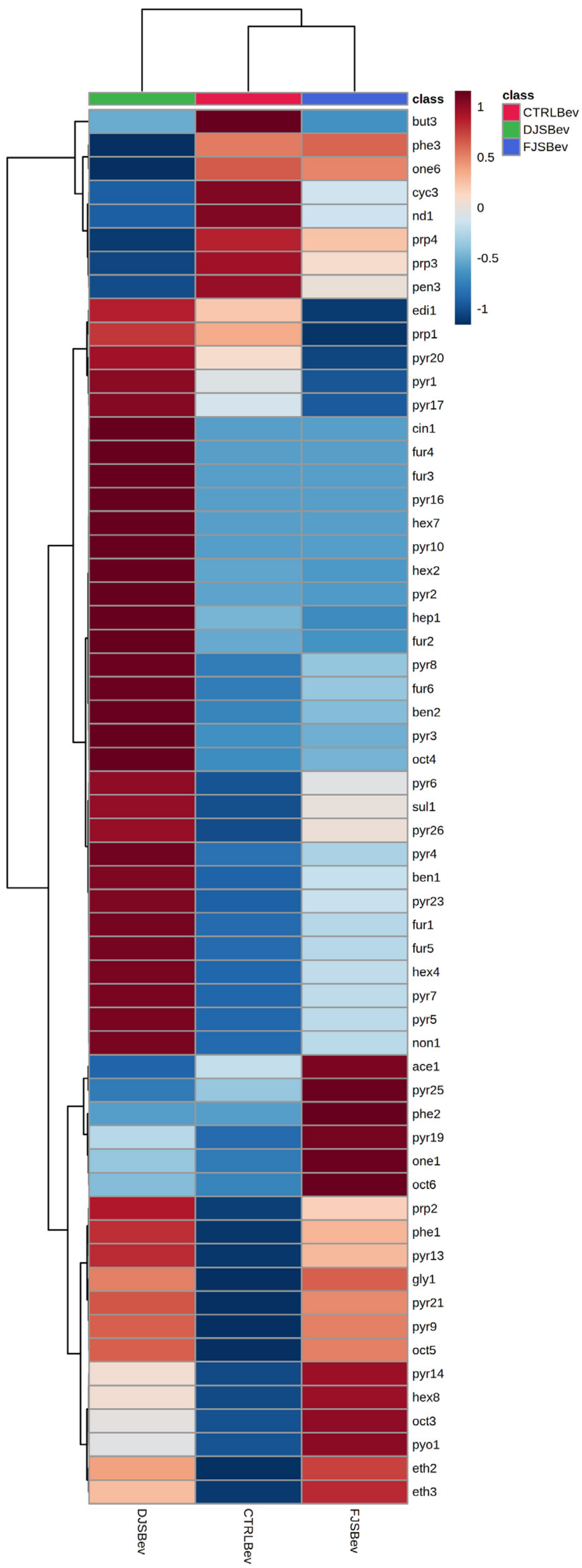

Fig. 4. Heatmap data showing the concentration of volatile compounds in the samples. The color scale represents the variation in the relative concentration of compounds in the beverage formulations, from low (blue) to high (red) content.

4. Discussion

4.1. Fermented jackfruit seed flour replaces natural chocolate aroma in an experimental beverage

In our study, GC/MS analysis detected the presence of 2,3 methylbutanoic acid (prp3), 2-phenylethanol (phe3), and acetic acid (ace1) in cocoa powder, FJS, CRTLBev, and FJSBev. Taken altogether, our findings suggest that fermentation is required to produce a chocolate aroma from jackfruit seeds. The same results about fermentation and chocolate aroma were found for cocoa beans (Al-Duais et al., 2009; Cempaka et al., 2021). These three compounds (prp3, phe3, and ace1) are typical odor-active constituents in cocoa products. Leucine is a limiting amino acid to obtain 2,3 methylbutanoic acid (prp3). In fermented samples such as cocoa, 2,3 methylbutanoic acid (prp3) is an important volatile compound (Liu et al., 2015; Owusu et al., 2012; Schwan and Wheals, 2004) that participates in further reactions such as aldol condensation, pyrazine formation, and oxidation. Oxidation of 3-methylbutanoic acid provides the precursor of 3-methybutanoate esters (Spada et al., 2021).

The compound 2,3 methylbutanoic acid (prp3) from the roasted cocoa mass was reported to be an aromatic constituent of milk chocolate (Liu et al., 2015; Owusu et al., 2012; Schwan and Wheals, 2004). The volatile compound 2-phenylethanol (phe3) was detected after alcoholic fermentation and is responsible for the high quality of cocoa products (Frauendorfer and Schieberle, 2008). It produces an intense honey, sweet, and fruity aroma, as well as flowery notes in cocoa products (Menezes et al., 2016). This could explain the chocolate aroma of the experimental FJS-added beverage developed in our study.

Fast-drying causes excess production of acids, including acetic acid (ace1), which negatively impacts the flavor, while very slow drying results in lower pH (Afoakwa, 2010; Kongor et al., 2016). In this study, the samples were controlled for appropriate drying to minimize and standardize drying-related effects.

The jackfruit seed flours tested herein showed different volatile profiles. FJS showed a low acetic acid (ace1) concentration, in contrast to alkaline and non-alkaline cocoa powder. The compounds 2-phenylethanol (phe3), ethyl acetate (ace2), propanoic acid, 2-methyl (prp3), and 3-Hydroxy-2-butanone (one5) were detected in FJS and cocoa samples, but not in DJS and natural cocoa. Propanoic acid (prp4) was only detected in FJS and alkaline cocoa samples.

The main purpose of the alkalization step is to generate numerous volatiles that contribute to the organoleptic properties and modify the color of cocoa powders (Sioriki et al., 2021). In our study, we found differences in chroma results between alkaline and non-alkaline cocoa powders. However, the chroma measurements of FJSBev and non-alkaline cocoa were not significantly different ($p > 0.05$). Spada et al. (2018) reported that the color of cappuccino formulations containing jackfruit seed flours did not affect their sensory acceptance by consumers. Spada et al. (2017) reported that FJS had an intense chocolate aroma and that sensory data indicated no preferences between jackfruit seed flours and cocoa powder ($p > 0.05$).

4.2. Similarities in the volatile profile of beverages containing cocoa powder and fermented jackfruit seeds

The main groups of volatile compounds identified in both CTRLBev and FJSBev were alcohols [1-octen-3-ol (oct4) and benzyl alcohol (ben2)]; aldehydes [benzaldehyde (ben1) and E-cinnamaldehyde (cin1)]; furans (fur1), and pyrazines [pyrazine, methyl (pyr2); pyrazine, ethyl (pyr5); pyrazine, 2-ethyl-6 (5)-methyl (pyr7); pyrazine, 2,6-dimethyl (pyr4); and pyrazine, 2,5-dimethyl (pyr3)] (Table 2). Benzyl alcohol (ben2) has been considered one of the main compounds responsible for the quality of cocoa products. Aldehydes, specifically from leucine, isoleucine, and valine, also play an important role in cocoa flavor (Kongor et al., 2016). E-cinnamaldehyde (cin1) is an aldehyde with a typical cinnamon aroma whose synthesis is associated with lignin and

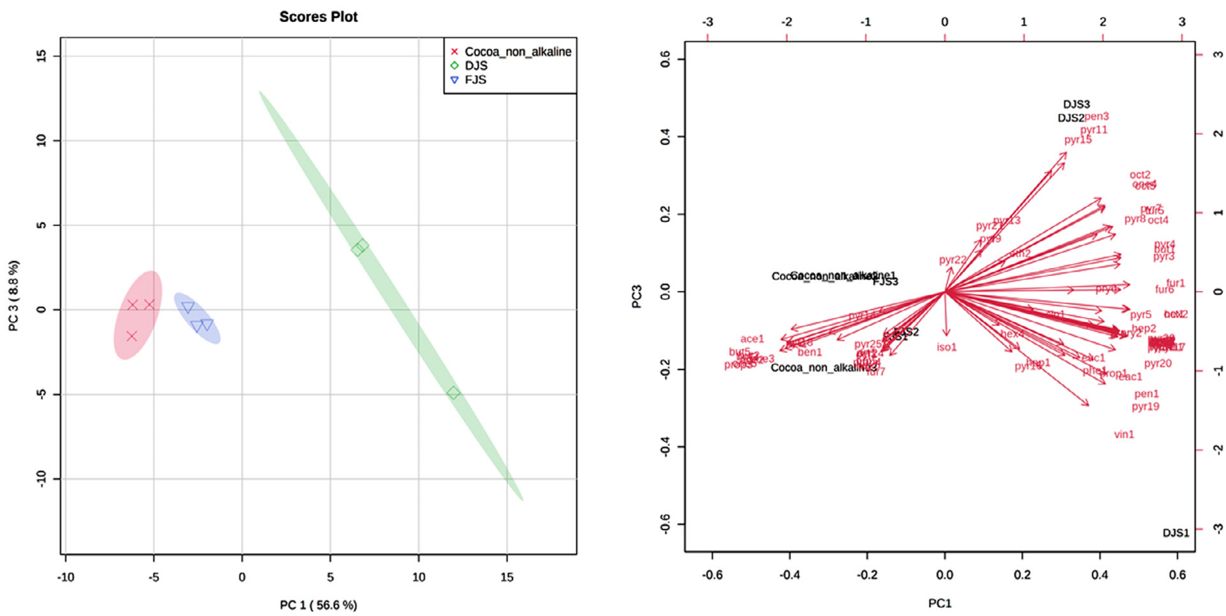

Fig. 5. A. Principal components analysis (PCA) of all volatile constituents (GC/MS) detected in non-alkaline cocoa powder, and dry and fermented jackfruit seed flours. B. Principal components analysis (PCA) of the projection of all volatile constituents (GC/MS) contained in non-alkaline cocoa powder, and dry and fermented jackfruit seed flours.

phenylalanine in the aldol-condensation process by benzaldehyde and acetaldehyde. The cinnamon aroma had a positive impact on overall impressions of cappuccino formulations (Spada et al., 2018). In the presence of glucose and glycine, aldehydes can produce pyrazines with a chocolate aroma.

Pyrazines and furans are the result of a wide variety of heterocyclic, carboxylic, and aliphatic compounds produced during the Maillard reaction. Maillard-derived furans can be affected by heating and pH. Moreover, amino acids and α-dicarbonyls generated in Strecker's intermediate stage are particularly important to produce aroma-active aldehydes and pyrazine derivatives (Perez-Locas and Yaylayan, 2010).

In our study, the content of methyl, dimethyl, ethyl, and ethyl-methyl pyrazines in CTRLBev and FJSBev was similar ($p > 0.05$). These Maillard derivatives have been commonly found in cocoa products, roasted coffee, roasted nut, beer, and malt. Essential amino acids (EAAs) were detected in FJS samples. EAAs possess a side chain with an α-amino group available to react with the electropositive centers of simple carbohydrates (hexose sugars are more available for interaction). These are necessary to produce a chocolate aroma during roasting by the Maillard reaction and Strecker's degradation. The natural presence of these pyrazines in FJS is remarkable and may be responsible for the similar volatile profile of FJS and cocoa beverages.

In the study of Spada et al. (2018) with experimental cappuccino formulations containing jackfruit seed flours, study participants referred to chocolate, cappuccino, cinnamon, coffee, and fermented as sensory descriptors. These attributes could be strongly associated with the odor-active volatiles described herein.

4.3. Odor-active constituents in beverage formulations containing fermented jackfruit seed flours and cocoa powder

Volatile compounds with cocoa descriptors (butter, cocoa, coffee, floral, fruit, green, honey, mushroom, nut, and roasted) and low threshold values (3 × 10–5 to 13 mg m^{-3}) were detected in FJSBev and CTRLBev (Table 2). This could be explained by the fact that Maillard reaction pathways producing roasted, nutty flavors require higher activation energy (Crafack et al., 2014). Maillard derivatives such as alkylpyrazines, which are found in roasted coffee, beer, or malt, are generally associated with unpleasant bitterness, as well as burnt and astringent tones (Kongor et al., 2016). Furans are associated with sweet, chocolate, and coffee aromas (Ito and Mori, 2004; Ledl and Schleicher, 1990). Phenylethanol produces a typical flowery and candy aroma in the sensory profiling of chocolate (Liu et al., 2015). This could also explain the chocolate flavor produced by roasted jackfruit seed flours, particularly fermented seeds (Spada et al., 2021). Aldehydes such as phenylacetaldehyde from phenylalanine produce honey, green, floral, and malty cocoa notes.

In our study, FJS was found to have a volatile profile very similar to that of cocoa powder, which is consistent with previous findings (Spada et al., 2021). We also found that alkaline and non-alkaline cocoa samples have a similar volatile profile and that ethyl-methyl pyrazines are more evident in alkaline cocoa. Hence, further research should test the alkalization of jackfruit seeds to increase the concentration of volatile compounds associated with chocolate descriptors.

5. Conclusions

To conclude, cocoa volatiles were identified in experimental beverages containing fermented jackfruit seed flours. The beverage formulation containing fermented jackfruit seeds showed more volatiles and odor-active constituents than that made of non-alkaline cocoa powder. Collectively, our data demonstrate that fermentation is critical to producing a chocolate aroma. Fermented jackfruit seed flours could be used as a partial or total additive to improve chocolate aroma in food formulations.

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Declaration of Competing Interest

The authors declare no conflict of interest.

Supplementary materials

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.fufo.2022.100158.

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