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Effect of fermentation time and drying temperature on volatile compounds in cocoa

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ABSTRACT

The effects of fermentation time and drying temperature on the profile of volatile compounds were evaluated after 2, 4, 6, and 8 fermentation days followed by drying at 60, 70 and 80 °C. These treatments were compared with dry cocoa controls produced in a Samoa drier and by a sun-drying process. A total of 58 volatile compounds were identified by SPME-HS/GC–MS and classified as: esters (20), alcohols (12), acids (11), aldehydes and ketones (8), pyrazines (4) and other compounds (3). Six days of fermentation were enough to produce volatile compounds with flavour notes desirable in cocoa beans, as well as to avoid the production of compounds with off-flavour notes. Drying at 70 and 80 °C after six fermentation days presented a volatile profile similar to the one obtained by sun drying. However, drying at 70 °C represents a lower cost. Given the above results, in the present study the optimal conditions for fermentation and drying of cocoa beans were 6 days of fermentation, followed by drying at 70 °C.

1. Introduction

The cocoa bean (*Theobroma cacao* L.) is one of main crops grown in the southwest of Mexico and this has been cultivated since prehispanic times. In 2010, a total of 61,344 ha were cultivated, producing 27,174 dry tons of cocoa beans (SIAP/SAGARPA, 2011). The States of Tabasco, Chiapas, Guerrero and Oaxaca are the main producers in Mexico, where cocoa processing is still carried out in the traditional way, from harvest and fermentation to drying.

The microbial fermentation and drying process are two major steps in the processing of cocoa beans and they are essential in the formation of flavour, which is an important parameter of quality in chocolate processing (Hii, Law, Cloke, & Suzannah, 2009b).

The fresh cocoa beans are enveloped in a sweet, white and mucilaginous pulp that represents approximately 40% of raw bean in wet weight and this pulp is a rich medium for microbial growth (Schwan & Wheals, 2004). The raw cocoa is usually fermented using the box method from 2 to 8 days depending of the variety and conditions of the cocoa (Hii, Law, & Cloke, 2009a). The spontaneous fermentation is developed by microorganisms transferred to the seeds from workers hands, surfaces and tools used for cutting the fruit and containers during fermentation. This process generates pulp juices with alcohols, acids and an increase of heat (Thompson, Miller, & Lopez, 2001).

Several fermenter microorganisms have been reported as volatile compounds producers during cocoa fermentation (Thompson et al., 2001). Schwan and Wheals (2004) reported that *Kloeckera apiculata* and *Saccharomyces cerevisiae* var. *chevalieri* were the most important producers of volatile compounds such as isopropyl acetate, ethyl acetate, 1-propanol, isoamyl alcohol, 2,3-butanediol, diethyl succinate and 2-phenylethanol. Furthermore, acetic and lactic acid, 2,3-butanediol and tetramethylpyrazine were produced by *Bacillus* spp. These bacteria also produce C_3–C_5 free fatty acids, found during aerobic fermentation, which are considered responsible for off-flavours in chocolate.

Aculey et al. (2010) reported that fermenting cocoa for less than 24 h and different methods of drying had high concentrations of volatile compounds such as 2-methylpropanal, 2,3-butanedione, 2-pentanol, methyl acetate, 2-heptanone, 2-pentyl propanoate, 1-pentanol, 2-methylbutanal, 3-methylbutanal, tetrahydro-2-methyl furan, 2-methyl-1-propanol and ethyl acetate. On the other hand, fermenting cocoa for more than 72 h presented high concentrations of propionic acid, linalool oxide, acetoin, 2-methylpropionic acid, 1-hidroxy-2-propanone, 3-methylbutanoic acid, acetic acid,

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2-phenylethyl acetate, 2,3,5,6-tetramethylpyrazine, 2-pentyl acetate, benzaldehyde, trimethylpyrazine, benzene ethanol, 3-methylbutyl acetate and linalool.

Alcohols, aldehydes and ketones have been reported as the major groups of compounds found in raw cocoa and at the beginning of the fermentation (1 or 2 days). However, alcohols, esters and acids (acetic acid mainly) were developed in the middle of fermentation (3–5 days); finally acids, esters and alcohols were the most important groups of volatile compounds at the end fermentation (6–8 days) (Rodriguez-Campos, Escalona-Buendía, Orozco-Avila, Lugo-Cervantes, & Jaramillo-Flores, 2011).

Traditionally, drying of fermented cocoa is performed by exposure to the sun. In this stage, the flavour development and the browning processes continue and the astringency, bitterness and acidity are reduced (Jinap & Thien, 1994). The drying process finishes when the moisture content is less than 8% in the beans. Sun drying is considered the best method to obtain the maximum flavour development (Jinap, Siti, & Norsiati, 1994). However, this method has disadvantages due to its long times and the labours required, producing cocoa with heterogeneous quality during rainy weather (Guehi, Zahouli, Ban-Koffi, Fae, & Nemlin, 2010). Rodriguez-Campos et al. (2011) reported that alcohols, esters and pyrazines contents increased during the sun drying process. Nevertheless, acids, aldehydes and ketones contents decreased.

Alternative drying methods have been introduced, such as artificial drying (Páramo, García-Alamilla, Salgado-Cervantes, Robles-Olvera, Rodríguez-Jimenes, & García-Alvarado, 2010). García-Alamilla, Salgado-Cervantes, Barel, Berthomieu, Rodríguez-Jimenes, and García-Alvarado (2007) found that artificially dried cocoa had a higher acidity than sun dried cocoa and the reduction of the volatile fatty acids (VFAs) content in artificial drying was lower than sun drying. However, other authors reported that VFAs content and pH of sun dried cocoa was not significant different compared to the artificially dried cocoa with six fermentation days (Guehi et al., 2010).

Some publications of artificially dried cocoa relate its quality with acidity, sensory and volatile composition (Guehi et al., 2010; Páramo et al., 2010). The temperature most commonly used for artificial drying is from 40 to 60 °C at laboratory conditions; although in large farm facilities the drying process is usually carried out at higher temperatures. A high drying temperature produces negative effects on flavour quality (Hii et al., 2009b). Solid phase microextraction (SPME) has been used for quantitative purposes in volatile compounds for different products, such as alcoholic beverages (Charry-Parra, DeJesus-Echevarria, & Perez, 2011), coffee (Korhonová, Hron, Klimcíková, Müller, Bednár, & Barták, 2009), sausages (Marco, Navarro, & Flores, 2007), milk (Jimenez-Alvarez et al., 2008), juice (Fan et al., 2009; Mirhosseini, Salmah, Nazimah, & Tan, 2007) and cocoa bean (Humston, Zhang, Brabeck, McShea, & Synovec, 2009). This technique has been reported to be cheap, solventless, fast and also has a high reproducibility, limits of detection and sensitivity (Balasubramanian & Panigrahi, 2011; Ducki, Miralles-Garcia, Zumbé, Tornero, & Storey, 2008; Howard, Mike, & Riesen, 2005).

In Mexico, artificial drying is used in large farm facilities in the season of high production and rainy weather. Mexican farmers use Samoa horizontal driers with hot air at 60–70 °C. The aromatic quality of cocoa obtained with the use of this drier has not been evaluated and correlated with the fermentation process. Little research relates the fermentation time and drying temperature with volatile compounds (Aculey et al., 2010). Nowadays, the optimal conditions in the fermentation and drying processes to obtain a high aromatic quality are necessary. Therefore, the aim of this research was to identify the volatile compounds in cocoa beans at different fermentation times and drying temperatures in order to improve the conditions in the processing of cocoa beans.

2. Materials and methods

2.1. Chemicals and standards

The compounds used as standards such as 3-methyl-1-butanol, 1-pentanol, 1-phenylethanol, benzyl alcohol, phenylethyl alcohol, 2-methylbutanal, 3-methylbutanal, acetophenone, 3-methyl-1-butanol acetate, ethyl hexanoate, 2-phenylethyl acetate, acetic, propionic, isobutyric, isovaleric, octanoic and nonanoic acids, 2,3-dimethylpyrazine, trimethylpyrazine, tetramethylpyrazine were all obtained from Sigma–Aldrich.

2.2. Fermentation and drying processes

Samples of cocoa beans of the Forastero variety were obtained from a large farm in Cunduacan, Tabasco, Mexico. The farmers bought the raw cocoa and a spontaneous fermentation was carried out with 1000 kg, within wooden boxes of 1 m^3 capacity, for 8 days at room temperature. The cocoa beans were manually turned up from one box to the other once per day, to obtain a uniform fermentation.

During fermentation, samples of 2 kg cocoa were taken at 48 h intervals (2, 4, 6 and 8 days of fermentation), frozen and transported to the laboratory. Every sample of cocoa beans was dried in a convection oven (San-Son, Plus HCX II) at three different temperatures: 60, 70 and 80 °C for 12, 8 and 6 h, respectively, to obtain a final moisture of 5–6%. Treatments for each cocoa sample were defined by choosing a drying temperature and a fermentation time per sample, as follows: 60-2 (60 °C drying temperature with two fermentation days), 4, 6, 8; 70-2, 4, 6, 8; and 80-2, 4, 6, 8.

In addition, two samples of fully fermented cocoa (8 days) and dried cocoa were obtained from the farm. One of the cocoa samples had been sun-dried at a temperature of 50 ± 2 °C and was chosen as the first control (Sun). The sun-drying process was done by placing the fermented cocoa on a concrete floor in 10 cm thick layers. Afterwards, the beans were mixed manually every day to obtain moisture of 7% during 5 days. Another fermented cocoa sample was dried in a Samoa drier, and it was considered the second control (Samoa). The artificial drying in the farms was carried out by placing layers of 14 cm of thickness on the perforated metal plates of the Samoa dryer with hot air at 65 °C for 12 h and mixed frequently.

2.3. Extraction of volatile compounds

The volatile compounds of cocoa samples (2.0 g) were extracted using the technique of solid phase microextraction in the headspace (SPME-HS) described by Rodriguez-Campos et al. (2011), using a fibre 50/30 μm divinylbenzene/carboxene/polydimethylsiloxane (DVB/CAR/PDMS) provided by Supelco to extract volatiles. The extraction conditions were previously optimised by combining the exposure time of the fibre (15, 30 and 45 min) at different temperatures (40, 50 and 60 °C). The optimal conditions were selected, where the highest number and abundance of volatile compounds appeared in raw, fermented, dried and roasted cocoa beans. The optimal conditions were 15 min in order to reach equilibrium, with a fibre exposition of 30 min to the samples of cocoa in the HS at 60 °C.

2.4. Separation and identification of volatile compounds

The volatile compounds were analysed by gas chromatography-mass spectrometry (GC–MS) (Hewlett Packard Model 5890 Series II, Palo Alto, Ca.), equipped with an Innowax capillary column (60 m ∗ 0.25 mm id ∗ 0.25 μm film thickness). The oven

temperature was set at 40 °C for 5 min, increased until 200 °C at a rate of 10 °C min^{-1}, and finally maintained at 200 °C for 30 min. The carrier gas was high purity helium at 0.7 ml min^{-1}. The splitless injection mode was at 240 °C (0.5 min). The selective mass detector was a quadrupole (Hewlett Packard, Model 5972), with an electronic impact ionisation system at 70 eV and at 260 °C. The identification of compounds was based on three criteria: (1) by comparing the mass spectra with the Wiley 275L library of mass spectra; (2) by comparing the retention index with literature data, and (3) whenever possible, the identification was confirmed by using pure standards of the components. Standard curves for quantification were obtained by preparing a solution with the different standard compounds in concentrations of 0.06, 0.125, 0.25, 0.5, 1.0, 2.0, 10 and 200 mg l^{-1}. The concentrations were calculated with a lineal regression equation from each standard compound, which had an R^2 from 0.977 to 0.9999. When a commercial standard was not available, quantification was performed using the slope obtained for a standard of an analogue compound that was structurally similar, but slightly different. This latter quantification method has been applied by Counet, Callemien, Ouwerx, and Collin (2002).

2.5. Statistical analysis

The concentrations of volatile compounds by functional group and individual compounds were tested with a two-way analysis of variance (ANOVA) to find significant differences between treatments, using a PROC GLM and the Tukey test. The statistical software used was SAS for Windows (SAS Institute Version 9.1, USA). The volatile compounds concentrations were subjected to principal component analysis (PCA) using Simca-P statistical software (Umetri AB, 7.1 version).

3. Results and discussion

3.1. Concentration of volatile compounds

In this research were identified a total of 58 compounds grouped into six main chemical groups (Table 1). The esters (20), alcohols (12) and acids (11) groups showed higher numbers of individual compounds than aldehydes and ketones (8), pyrazines (4) and other compounds (3). A similar number of compounds were found by Frauendorfer and Schieberle (2008) in fermented and dried Criollo cocoa. They found 9 alcohols, 11 aldehydes and ketones, 4 esters, 6 acids, and 6 pyrazines.

The total concentrations of acids, aldehydes and ketones, alcohols and esters were higher than the concentrations of pyrazines and other compounds (Fig. 1a–f).

3.1.1. Concentration of alcohols

Some indentified alcohols (Table 1) are responsible for producing desirable flavour notes, i.e. 3-methyl-1-butanol, 2-heptanol and 2-phenylethanol (Ducki et al., 2008; Jinap, Wan-Rosli, Russly, & Nordin, 1998). The total alcohol concentration increased up to six fermentation days at all drying temperatures, and after that a decrease was observed. No significant differences were found at 70 and 80 °C in all fermentation times ($p > 0.05$) (Fig. 1a). Portillo et al. (2009) reported that the concentrations of alcohols decreased during the sun drying process. High alcohol contents are desirable to obtain cocoa products with flowery and candy notes (Aculey et al., 2010; Frauendorfer & Schieberle, 2008).

The concentrations of 3-methyl-1-butanol and 2-methyl-1-propanol had a significant decrease when the fermentation time increased, and this effect was independent of the drying temperature (Fig. 2a and b). The concentration of 3-methyl-1-butanol in the Samoa control was significantly higher than the one in all the experimental samples and the Sun control. The highest concentration of 2-methyl-1-propanol was found after two fermentation days with a significant increase at high drying temperatures; 60 °C with 0.3 mg kg^{-1}, 70 °C with 0.65 mg kg^{-1} and 80 °C with 0.8 mg kg^{-1}. Oberparleiter and Ziegleder (1997) reported an interval of 2–16 mg kg^{-1} for 3-methyl-1-butanol in fermented cocoa from different countries.

The 3-methyl-1-butanol is an amyl alcohol and it can be oxidised to 3-methyl-1-butanol acetate. The esterification of amyl alcohols to amyl acetates could be used as a fermentation index (Oberparleiter & Ziegleder, 1997; Rodriguez-Campos et al., 2011), and it produces malty and chocolate notes (Table 1) (Afoakwa, Paterson, Fowler, & Ryan, 2008).

The benzyl alcohol and 2-phenylethanol provide flowery flavour notes (Jinap et al., 1998). We found that the concentration of these compounds significantly increased with an increase of fermentation time at all temperatures. However, no significant differences were observed at days 6 and 8 as compared to the controls (Fig. 2c and d). The contents of these two alcohols were significantly higher in the Samoa than in the Sun control.

The benzyl alcohol showed an average concentration of 1.5 mg kg^{-1} after eight fermentation days and in the two controls (Samoa and Sun). Ziegleder (1991) reported a lower concentration (0.1–0.5 mg kg^{-1}) of benzyl alcohol in unroasted cocoa. In addition, we observed that the 2-phenylethanol had 2 mg kg^{-1} of average concentration after eight fermentation days, which was similar from Samoa and Sun controls. Frauendorfer and Schieberle (2008) reported 2-phenylethanol at a concentration of 3.5 mg kg^{-1} in unroasted cocoa. This last compound was reported to be the most odour-active compound among the neutral/basic fraction in the fermented and dried cocoa aroma (Frauendorfer & Schieberle, 2008).

3.1.2. Concentration of aldehydes and ketones

The total concentration of aldehydes and ketones increased significantly with an increase in fermentation time at 60 °C. The same effect was observed at 70 °C and 80 °C, but no significant differences were found among fermentation days ($p > 0.05$) (Fig. 1b). Total concentration (average of 11 mg kg^{-1}) of aldehydes and ketones was lower in both controls than in most of the experimental samples. The treatments of 60-6, 70-6, 70-8 and all treatments at 80 °C had significantly higher concentrations than the controls, with an interval from 20 to 25 mg kg^{-1} ($p < 0.05$) (Fig. 1b). A high concentration of aldehydes and ketones is favourable for cocoa quality, producing fruity and flowery notes, i.e. 2-methylbutanal and 3-methylbutanal (Serra-Bonvehí, 2005).

2-Methylbutanal and 3-methylbutanal could be formed from precursors such as isoleucine and leucine by lactic acid bacteria during fermentation (Jinap et al., 1994). These compounds produce malty and chocolate flavour notes in unroasted and roasted cocoa (Frauendorfer & Schieberle, 2008; Schnermann & Schieberle, 1997). Overall, we observed that the concentration of 2-methylbutanal was not affected by fermentation time and drying temperature (Fig. 3a). The 70-8 treatment produced the highest concentration (0.75 mg kg^{-1}), and it was not significantly different to other fermentation times. All treatments had a significantly higher concentration than the Sun control ($p < 0.05$) (Fig. 3a). The 2-methylbutanal has been reported to have a similar concentration (0.56 mg kg^{-1}) in unroasted cocoa (Frauendorfer & Schieberle, 2008).

The changes in the concentration of 3-methylbutanal were significantly different during the fermentation period at 60 and 70 °C, but no significant differences were observed between 6 and 8 fermentation days at both temperatures (Fig. 3b). At these fermentation times and all drying temperatures, the 3-methylbutanal concentrations were significantly higher than the Sun control with 0.7 mg kg^{-1} ($p < 0.05$), but no significant differences were observed

Table 1
Volatile compounds identified during different fermentation times and drying temperatures in cocoa.

Number	Compound	Odour description[a]	Sample found[b]	Identification[c]
Alcohols				
1	1-Propanol	Sweet, candy	60-2–60-6, 70-2, 70-4, 80-2, 80-4	MS-IK
2	2-Methyl-1-propanol	Wine	All	MS-IK
3	1-Butanol		60-2, 60-4, 80-2	MS-IK
4	3-Methyl-1-butanol	Malty, chocolate	All	MS-IK-STD
5	1-Pentanol		70-2, 70-4, 80-2, 80-4	MS-IK-STD
6	3-Methyl-3-butanol		70-6, 70-8, 80-2, 80-4	MS-IK
7	2-Heptanol	Sweet, citrusy	Sun, 70-2	MS-IK
8	2,3-Butanediol		All	MS-IK
9	1,3-Butanediol		All	MS
10	1-Phenylethanol	Honey, floral	Sun, Samoa, 60-4–60-8, 70-2–70-8, 80-2–80-8	MS-IK-STD
11	Benzyl alcohol	Sweet, flowery	Sun, Samoa, 60-4–60-8, 70-2–70-8, 80-2–80-8	MS-IK-STD
12	2-Phenylethanol	Honey, flowery	All	MS-IK-STD
Aldehydes and ketones				
13	2-Methylbutanal	Malty, chocolate	All	MS-IK-STD
14	3-Methylbutanal	Malty, chocolate	All	MS-IK-STD
15	2,3-Butanedione	Buttery	All	MS-IK
16	2-Heptanone	Fruity, flowery	Sun, 60-2, 70-2–70-8, 80-2–80-8	MS-IK
17	Acetoin	Butter, cream	All	MS-IK-STD
18	2-Nonanone		Sun, 70-2, 80-4–80-8	MS-IK
19	Acetophenone	Flowery, sweet	All	MS-IK-STD
20	2-Phenyl-2-butenal	Sweet, roasted	60-6, 60-8, 70-8, 80-4	MS-IK
Esters				
21	Methyl acetate		All	MS-IK
22	Ethyl acetate	Pineapple	All	MS-IK
23	Methyl formate		60-8, 70-2, 70-6, 70-8, 80-2, 80-6, 80-8	MS
24	Ethyl formate		60-2, 70-4–70-8, 80-4	MS
25	Isobutyl acetate	Fruity	Sun, Samoa, 60-2–60-6, 70-2–70-6, 80-2–0-8	MS-IK
26	Ethyl 2-methylbutanoate	Fruity	Sun, Samoa, 70-4, 70-6	MS-IK
27	Ethyl 3-methylbutanoate	Fruity	Sun, Samoa	MS-IK
28	2-Pentyl acetate	Fruity	All	MS-IK
29	3-Methyl-1-butanol acetate	Banana	All	MS-IK-STD
30	Ethyl hexanoate	Fruity	All	MS-IK-STD
31	Methyl lactate		60-2–60-6, 70-2–70-6, 80-2–80-8	MS
32	Ethyl lactate	Fruity	All	MS-IK
33	Ethyl octanoate	Fruity, flowery	All	MS-IK
34	Ethyl decanoate	Pear, grape	Sun, Samoa, 60-2–60-8, 70-2, 70-8, 80-2	MS-IK
35	Benzyl acetate	Floral, jasmine	60-6, 60-8, 70-6, 70-8	MS-IK
36	Ethylphenyl acetate	Fruity, sweet	All	MS-IK
37	2-Phenylethyl acetate	Honey, flowery	All	MS-IK-STD
38	Isoamyl benzoate	Balsam, sweet	70-2–70-6, 80-2–80-8	MS
39	Ethyl cinnamate	Sweet, cinnamon-like	60-8, 80-4–80-8	MS-IK
40	Ethyl palmitate	Waxy, green	Samoa, 60-4–60-8, 80-4	MS-IK
Acids				
41	Acetic acid	Sour, viniegra	All	MS-IK-STD
42	Propanoic acid	Pungent, rancid	All	MS-IK-STD
43	Isobutyric acid	Rancid, butter	All	MS-IK-STD
44	Isovaleric acid	Sweat, rancid	All	MS-IK-STD
45	Hexanoic acid	Sweat, pungent	Sun, Samoa, 60-4–60-8, 70-2–70-8, 80-2–80-8	MS-IK
46	Heptanoic acid	Rancid, sour	Sun, Samoa, 60-6, 60-8, 70-8, 80-4–80-8	MS-IK
47	Octanoic acid	Sweat, fatty	All	MS-IK-STD
48	Nonanoic acid	Green, fatty	All	MS-IK-STD
49	Decanoic acid	Rancid, fatty	Samoa, 60-4–60-8, 70-4–70-8, 80-4, 80-8	MS-IK
50	Undecanoic acid		Sun, 60-2–60-8, 70-2–70-8, 80-4	MS
51	Dodecanoic acid	Metal	Sun, Samoa, 60-2, 80-6, 80-8	MS-IK
Pyrazines				
52	2,3-Dimethylpyrazine	Caramel, cocoa	Samoa, 60-6, 60-8, 70-4–70-8, 80-4–80-8	MS-IK-STD
53	2,3,5-Trimethylpyrazine	Cocoa, roasted	All	MS-IK-STD
54	2,3,5,6-Tetramethyl-pyrazine	Roasted, chocolate	All	MS-IK-STD
55	2,3,5-Trimethyl-6-ethylpyrazine	Candy, sweet	Samoa, 60-8, 70-4–70-8, 80-4– 808	MS-IK-STD
Others				
56	2-Methoxy phenol	Smoky, sweet	Sun, Samoa, 60-6, 60-8, 70-6, 70-8, 80-6, 80-8	MS-IK
57	2-Acetyl-1H-pyrrole	Chocolate, hazelnut	60-6, 60-8, 70-2–70-8, 80-2–80-8	MS-IK
58	Phenol	Smoky	60-8, 70-8, 80-8	MS-IK

[a] Obtained from literature
[b] 60, 70 and 80 means drying temperatures (°C); −2, 4, 6, and 8 means fermentation days; Samoa and Sun was the controls.
[c] MS = mass spectrometry, IK = Kovats index, STD = standard pure compound.

with the Samoa control (Fig. 3b). In unroasted cocoa, 3-methylbutanal was found at a concentration of 1.6 mg kg^{-1} and this compound showed the highest aroma activity in the unroasted and roasted cocoa (Frauendorfer & Schieberle, 2008).

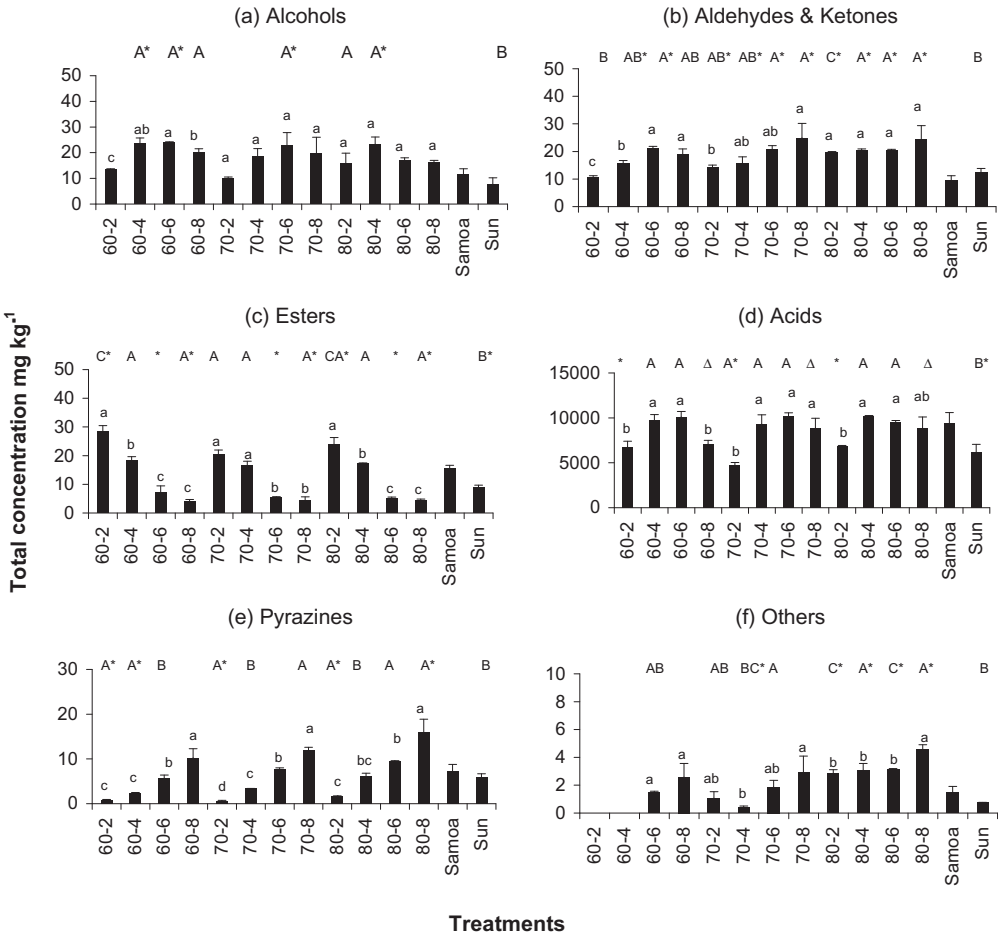

Fig. 1. Total concentrations of volatile compounds found in cocoa at different fermentation times and drying temperatures by functional group. Bars are ±standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control. Δ means that no significant difference was found between treatments and the two controls ($p < 0.05$).

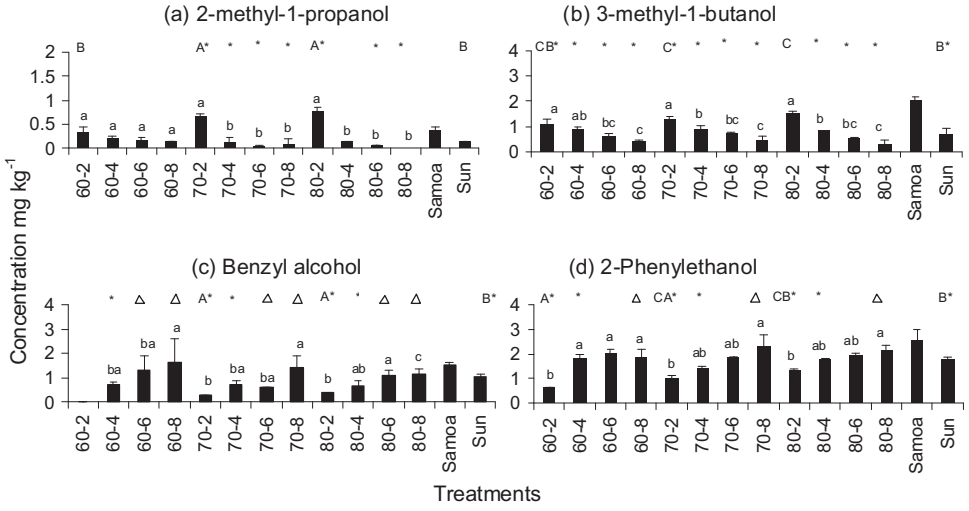

Fig. 2. Concentrations of some alcohols found in cocoa at different fermentation times and drying temperatures. Bars are ±standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control. Δ means that no significant difference was found between treatments and the two controls ($p < 0.05$).

In addition, we found that acetoin had the highest concentration among aldehydes and ketones, with an interval of 7–17 mg kg^{-1} (Fig. 3c). The concentration of acetoin was significantly raised up to six fermentation days at 60 °C. However, no significant

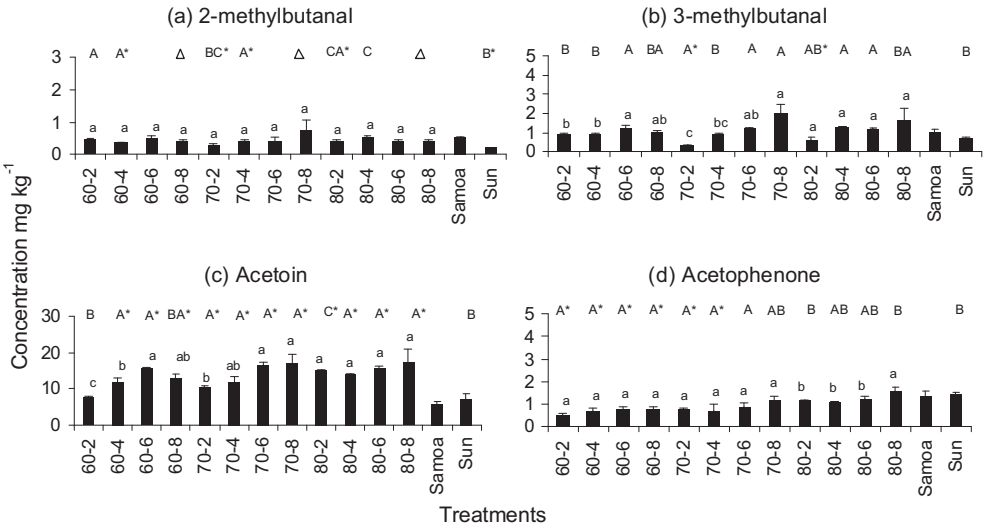

Fig. 3. Concentrations of some aldehydes and ketones found in cocoa at different fermentation times and drying temperatures. Bars are ± standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control. Δ means that no significant difference was found between treatments and the two controls ($p < 0.05$).

differences were observed between 6 and 8 fermentation days at all temperatures. Overall, the concentration of acetoin was significantly higher in all the experimental samples as compared to the Samoa and Sun controls ($p < 0.05$). Acetoin could be produced from piruvate and butanodiol as precursors during alcoholic fermentation (Pretorius, 2000), and it appears to be a precursor of tetramethylpyrazine (Hashim, Jinap, Muhammad, & Ali, 1999).

In this study, the acetophenone concentration was not affected by an increase of fermentation time at 60 and 70 °C. However, there was a significant increase from 6 to 8 fermentation days at 80 °C. The treatments with an acetophenone concentration similar to Sun and Samoa were 70-8 and all treatments at 80 °C with values of 1.2 and 1.3 mg kg^{-1}, respectively (Fig. 3d). Serra-Bonvehí (2005) reported that acetophenone had the highest concentration in roasted cocoa with an interval 1.6–3.8 mg kg^{-1}, this compound produces floral and sweet flavour notes.

The aldehydes and ketones were present in high concentrations at 6 and/or 8 fermentation days. The compounds 2-methylbutanal and 3-methylbutanal, which produce a desirable note, were found at their highest concentration at 70 °C. The acetoin and acetophenone did not show significant differences between 70 and 80 °C with 6 and 8 fermentation days. All this suggests that the best conditions to obtain desirable aldehydes and ketones were a temperature of 70 °C and a fermentation time of 6 or 8 days.

3.1.3. Concentrations of esters

Esters are correlated to fruity flavour notes and represent the second most important group of volatile compounds after the pyrazines in roasted cocoa nib (Jinap et al., 1998). Total concentration of esters significantly decreased from 28 to 4 mg kg^{-1} with an increase of fermentation time, but there were not significant differences between drying temperatures. Overall, the lowest total ester concentration was observed in the last stage of fermentation (6 and 8 days) without finding significant differences. In addition, controls Samoa and Sun showed a significantly higher concentration than these treatments ($p < 0.05$) (Fig. 1c).

We found that the concentrations of ethyl acetate and 3-methyl-1-butanol acetate significantly decreased during fermentation time at all temperatures, but no significant differences were observed between 6 and 8 fermentation days (Fig. 4a and b) ($p < 0.05$). The concentrations of ethyl acetate at these days were significantly lower than Samoa and Sun (3.5 and 2.0 mg kg^{-1}, respectively). Similarly, the 3-methyl-1-butanol acetate showed a significantly lower concentration in all treatments as was compared to the Samoa and Sun controls. Aculey et al. (2010), reported that the ethyl acetate concentration decreased and 3-methyl-1-butanol acetate increased. In this research, we observed that the content of 3-methyl-1-butanol acetate decreased and the 3-methylbutanal had a high concentration (up to 2 mg kg^{-1}) (Fig. 3b). It is possible that 3-methyl-1-butanol was oxidised to 3-methylbutanal producing a high concentration, while 3-methylbutanal probably was not esterified to 3-methyl-1-butanol acetate (Figs. 2a, 3b, 4b). In the fermentation process it is advisable to avoid the esterification of amyl alcohols to amyl acetates, because the presence of these compounds and low concentrations of methyl-1-butanols are considered as indicators by the flavour defects index (Oberparleiter & Ziegleder, 1997).

The average concentration (0.75 mg kg^{-1}) of ethylphenyl acetate was significantly higher in Samoa and Sun controls than in all treatments ($p < 0.05$). The changes in concentration of ethylphenyl acetate (an average of 0.23 mg kg^{-1}) were not significantly different over the fermentation period at the three drying temperatures (Fig. 4c). Serra-Bonvehí (2005) reported ethylphenyl acetate as one of the principal components of cocoa aroma, with fruity flavour notes and similar concentrations (0.35–1.87 mg kg^{-1}) to the ones found in the present study.

Furthermore, the 2-phenylethyl acetate concentration increased during fermentation at all temperatures, but these changes were not significantly different between 4, 6 and 8 fermentation days (Fig. 4d) ($p < 0.05$). The 2-phenylethyl acetate concentrations in Samoa (1.9 mg kg^{-1}) and Sun (1.6 mg kg^{-1}) were significantly higher than all treatments (Fig. 4d) ($p < 0.05$). Frauendorfer and Schieberle (2008) reported 1 mg kg^{-1} from 2-phenylethyl acetate in unroasted and roasted cocoa.

The production of this ester can be a result of yeast metabolism during the fermentation process, which produces key cocoa aromas such as flowery and honey flavour notes (Aculey et al., 2010; Frauendorfer & Schieberle, 2008).

It is beneficial for aromatic cocoa quality to have 2-phenylethyl acetate and ethylphenyl acetate in high concentrations, due to the flavour notes associated with them. We found the highest concentration of these compounds at 6 and 8 days, together with low

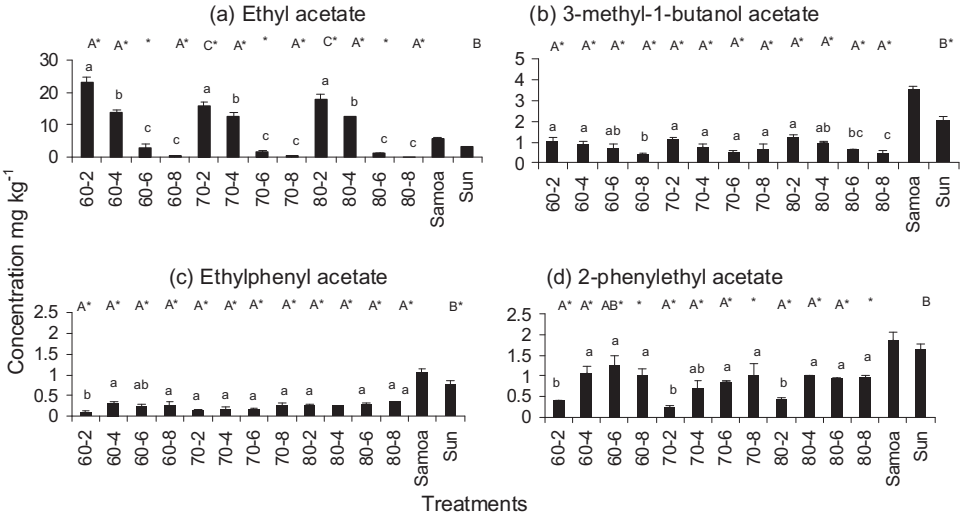

Fig. 4. Concentrations of some esters found in cocoa at different fermentation times and drying temperatures. Bars are ± standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as were compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control ($p < 0.05$).

concentrations of 3-methyl-1-butanol acetate, which is considered a flavour defect in cocoa products (Oberparleiter & Ziegleder, 1997). In this case, we might suggest 6 or 8 fermentation days, regardless of the drying temperature.

3.1.4. Concentration of acids

Frauendorfer and Schieberle (2008) reported that some short-chain carboxylic acids, particularly acetic and isovaleric, were dominant in the aroma of unroasted Criollo cocoa. In this research, the total concentration of acids was significantly higher than all the other chemical groups (Fig. 1d). The total acids concentration increased significantly at the beginning of fermentation (2 and 4 days) at the three drying temperatures. However, at the end of this process (6 and 8 days), no significant differences at 70 and 80 °C were found (Fig. 1d) ($p < 0.05$). These increases in organic acids concentration are the result of the metabolisms of sugars contained in the pulp of cocoa (Serra-Bonvehí, 2005; Thompson et al., 2001). During fermentation, some acids such as acetic acid can be diffused into the cocoa bean producing a decrease in the pH (Thompson et al., 2001).

The highest concentrations of acids were found in the treatments 60-6, 70-6 and 80-4 (10,114, 10,185 and 10,152 mg kg^{-1}, respectively). These treatments and the Samoa control were not significantly different. However, the concentration in the Sun control was significantly lower as compared to the Samoa (Fig. 1d) ($p < 0.05$).

It is known that acetic acid is produced by the biochemical synthesis from the oxidation of ethanol during the first stages of fermentation (Schwan & Wheals, 2004). We observed that the acetic acid concentration significantly increased up to four fermentation days at all temperatures, and after 6 days a decrease was observed. No significant differences were found after 6 and 8 fermentation days with 70 and 80 °C (Fig. 5a). The treatments 60-6, 70-6, 80-4 and the Samoa control (9576, 9772, 9789 and 8769 mg kg^{-1}, respectively) had significantly higher acetic acid concentrations than the Sun control ($p < 0.05$).

Jinap and Thien (1994) found an acetic acid concentration of 2971 mg kg^{-1} in oven-dried cocoa and 675 mg kg^{-1} in sun-dried. These concentrations were lower than the concentrations reported here. However, Holm and Aston (1993) reported concentrations from 1300 to 11,800 mg kg^{-1} in dried cocoa from different countries.

Acetic acid has been associated with sour and vinegar-like notes and it is considered the highest odour-active compound in unroasted and roasted cocoa (Afoakwa, Paterson, Fowler, & Ryan, 2009; Frauendorfer & Schieberle, 2006). Frauendorfer and Schieberle (2008) reported that during the roasting process, 70% of the acetic acid concentration was eliminated.

In addition, the isobutyric acid concentrations (193 mg kg^{-1}) were highest at 60 °C (Fig. 5b). An increase in fermentation time caused a rise in isobutyric concentration. However, no significant differences were observed between 4, 6 and 8 days of fermentation at 60 and 80 °C. The lowest concentrations of this compound were produced at 70 °C at all fermentation times, where the treatment at 8 days of fermentation had 103 mg kg^{-1} (Fig. 5b). Jinap and Dimick (1990) reported isobutyric acid concentrations from 11 to 77 mg kg^{-1} in fermented and dried cocoa. This acid produces off-flavour notes such as rancid, butter and hammy (Serra-Bonvehí, 2005).

The concentration of isovaleric acid had a significant increase when the fermentation time increased, independently of drying temperature (Fig. 5c). No significant differences were observed between the treatments and the Samoa control. The highest concentration (an average of 170 mg kg^{-1}) was found after 8 days of fermentation at the three temperatures and these concentrations were significantly higher than the Sun control (Fig. 5c). Jinap and Thien (1994) reported 101 mg kg^{-1} of isovaleric acid in oven-dried cocoa at 60 °C and 30 mg kg^{-1} in sun-dried cocoa. Isovaleric acid is an undesirable compound that produces rancid smelling (Serra-Bonvehí, 2005).

Finally, the propionic acid concentrations showed no significant differences between drying temperatures (Fig. 5d). This acid increased its concentration from 21 to 90 mg kg^{-1} with an increase in the fermentation time. However, only at 80 °C was this increase significant different as compared to fermentation time (Fig. 5d). The propionic acid produces rancid and pungent undesirable notes (Serra-Bonvehí, 2005). Jinap and Thien (1994) reported a value 42 mg kg^{-1} in artificial dried cocoa at 60 °C. Jinap and Dimick (1990) also reported 289 and 194 mg kg^{-1} of propionic acid in fermented and dried cocoa from Guatemala and Malaysia, respectively.

The isovaleric, isobutyric and propionic acids are produced by *Bacillus* spp. at the end of fermentation. However, over-fermentation may occur with large fermentation times, increasing the

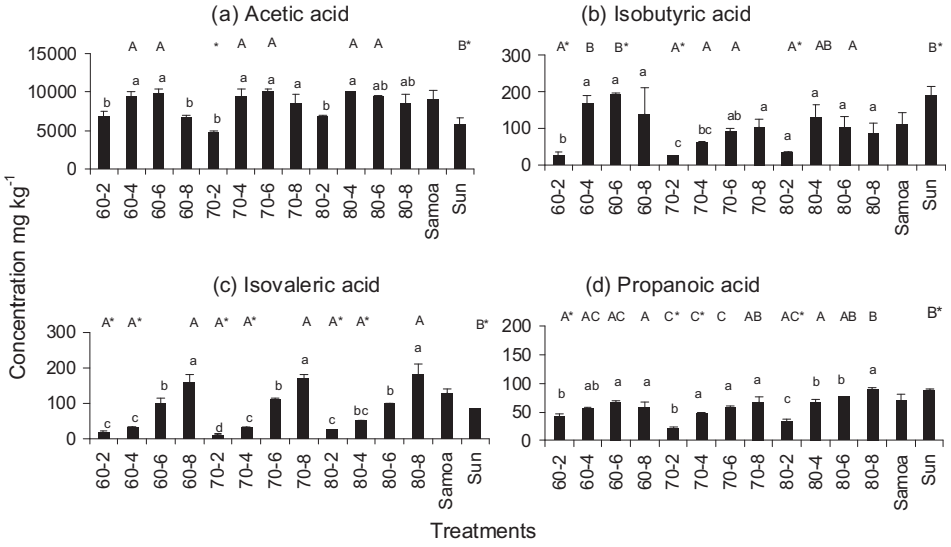

Fig. 5. Concentrations of some acids found in cocoa at different fermentation times and drying temperatures. Bars are ± standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control ($p < 0.05$).

concentration of these acids and their off-flavour notes. We did not find differences between 6 and 8 fermentation days in acetic and isobutyric acid concentration. Also, the isovaleric and propionic acid presented lower concentrations at day 6 as compared to day 8. Therefore, we suggest to stop the fermentation at 6 days to avoid the increase in concentration of these acids. We also recommend a drying temperature of 70 °C because the lowest concentration of isobutyric acid was found at this temperature.

3.1.5. Concentration of pyrazines

The group of pyrazines is one of the most important volatile compounds in roasted cocoa. Serra-Bonvehí (2005) mentioned that pyrazines represented 40% of the aroma in roasted cocoa. In the present study, the total concentration of pyrazines increased significantly during fermentation time at all drying temperatures (Fig. 1e) ($p < 0.05$). The controls were not significantly different regarding total concentration of pyrazines ($p < 0.05$). This suggests that sun-drying and the Samoa drier produce similar pyrazines concentration.

We only found three pyrazines, i.e. tetramethylpyrazine, trimethylpyrazine and 2,3-dimethylpyrazine (Table 1) in the samples under study. The first one, tetramethylpyrazine had a significant increase from 0.9 to 10.6 mg kg^{-1} during fermentation at all drying temperatures (Fig. 6a) ($p < 0.05$). Ramli, Hassan, Said, Samsudin, and Idris (2006) reported that tetramethylpyrazine represented 90% of the total concentration of pyrazines with an interval of 0.13–7.57 mg kg^{-1} in roasted cocoa at different temperatures and times of roasting. In this research, the highest concentrations of tetramethylpyrazine were found after 6 and 8 days of fermentation. Nevertheless, no significant differences were observed between the three drying temperatures. Hashim et al. (1999) found that the highest concentrations of tri- and tetramethylpyrazine were found at 60–70 °C drying temperature, while at 80 °C the concentration decreased. Tetramethylpyrazine is one of the main components of cocoa aroma and is responsible for the nutty, roasted and chocolate flavour notes (Afoakwa et al., 2009).

The changes in concentration of the second one, the trimethylpyrazine (from 0.05 to 3.3 mg kg^{-1}), were significantly different for different fermentation times at all drying temperatures (Fig. 6b) ($p < 0.05$). Hashim et al. (1999) reported the lowest concentration to this compound from 0.02 to 1.2 mg kg^{-1} and found the highest concentration (1.2 mg kg^{-1}) near 70 °C in dried cocoa. We found the highest concentrations with 6 and 8 days of fermentation and no significant differences were observed between these fermentation times at both 70 and 80 °C. The concentration of trimethylpyrazine in the Samoa control was significantly higher (1.7 mg kg^{-1}) than in the Sun control with 0.3 mg kg^{-1} (Fig. 6b) ($p < 0.05$). The concentration of trimethylpyrazine was reported from 0.35 to 5.4 mg kg^{-1} in roasted cocoa at different temperatures and times of roasting, and it was proposed as an indicator for the roasting degree (Ramli et al., 2006).

The last pyrazine found was 2,3-dimethylpyrazine, which increased significantly in concentration with an increase of fermentation time at the three drying temperatures (Fig. 6c) ($p < 0.05$). This compound was not found in the Sun control. The highest concentration from 2,3-dimethylpyrazine was observed after eight fermentation days, but no significant differences were found between 6 and 8 fermentation days. The 2,3-dimethylpyrazine has been reported in fermented cocoa (Jinap et al., 1994).

Tetramethylpyrazine and trimethylpyrazine were reported as compounds from microbiological origin produced at the end of fermentation by *Bacillus subtilis* and *Bacillus megatrium* (Jinap et al., 1994; Schwan & Wheals, 2004). However, the majority of pyrazines originated from the Strecker degradation in Maillard reactions. The α-aminoketones are precursors for pyrazines, oxazoles and thiasoles. In the case of alkylpyrazines, the most direct route for their formation is thought to be the self-condensation of α-aminoketones, or condensation with other aminoketones (Mottram, 2007). Furthermore, pyrazines are dependent on heat and an increase in drying temperature produces a rise in pyrazine concentrations, apparently due to the presence of some precursors, i.e. diacetyl and acetoin, which are precursors of tetramethylpyrazine (Hashim et al., 1999).

3.1.6. Concentration of other compounds

The compounds 2-methoxyphenol, 2-acetyl-1-pyrrole and phenol were also identified in the samples (Table 1). The total concentration of this chemical group had a significant increase at the end of fermentation (8 days) at all drying temperatures (Fig. 1f) ($p < 0.05$), with total concentrations of 0.9, 0.8 and 1.0 mg kg^{-1} for 60, 70 and 80 °C, respectively.

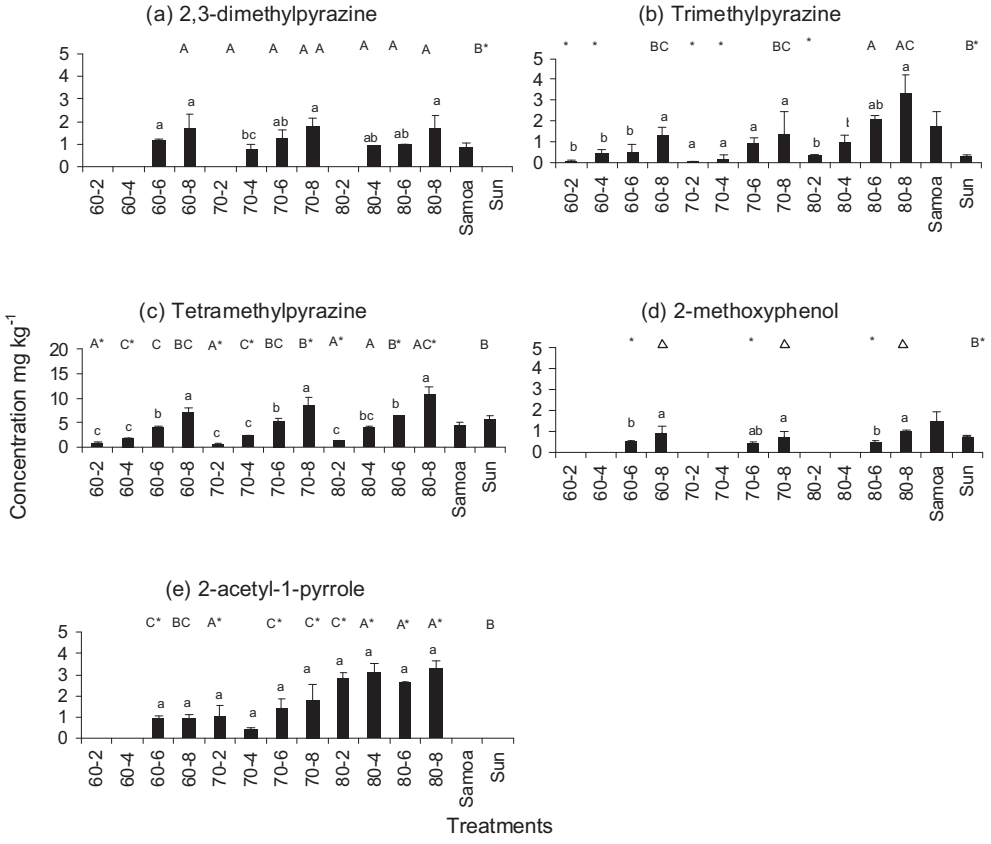

Fig. 6. Concentrations of some pyrazines and other compounds found in cocoa beans at different fermentation times and drying temperatures. Bars are ± standard deviation. $N = 3$. Different lowercase letters indicate significant differences between fermentation times at the same temperature. Different capital letters indicate significant differences between drying temperatures at the same time as compared to the Sun control. ∗ indicates significant differences between the treatment and the Samoa control. Δ means that no significant difference was found between treatments and the two controls ($p < 0.05$).

We observed 2-methoxyphenol only at the end of fermentation (6 and 8 days) at the three studied temperatures (Fig. 6d). However, after 6 days of fermentation we observed the significantly lowest concentration of this compound. The treatments after 8 days of fermentation with three drying temperatures were not significantly different as compared to the controls (Fig. 6d) ($p < 0.05$). The control Samoa had the higher concentration of 2-methoxyphenol (1.5 mg kg^{-1}) as was compared to the other treatments. Serra-Bonvehí and Venture (1998) reported similar concentrations from 2-methoxyphenol with an interval of 1.75 to 3.22 mg kg^{-1} in fermented and dried cocoa. The phenolic compounds can be produced during drying (by smoke contamination) or during storage of cocoa beans and they are correlated with smoky flavour notes in unroasted and roasted cocoa (Jinap et al., 1998; Serra-Bonvehí & Venture, 1998). Phenolic compounds are undesirable in cocoa products and are not normally present in good quality cocoa (Jinap et al., 1998).

Another compound identified in this study was 2-acetyl-1-pyrrole; it was present only in the experimental samples and not in the controls (Fig. 6e). Its concentration increased as drying temperatures increased, but these changes were not significant with respect to fermentation time (Fig. 6e). The treatments at 80 °C had the highest concentrations of 2-acetyl-1-pyrrole. This compound is produced from proline by Streker degradation during Maillard reaction and contributes many flavour notes desirable in roasted cocoa, i.e. caramel, chocolate and roasted (Afoakwa et al., 2009; Mottram, 2007).

In addition, the fermentation time showed significant differences on the concentration of esters ($p < 0.0001$), pyrazines ($p = 0.0004$) and others compounds ($p = 0.0296$), while drying temperature had a significant effect on alcohols ($p = 0.0081$), esters ($p < 0.0001$) and other compounds ($p = 0.0008$). However, the interaction of fermentation time with drying temperature only had a significant effect on the esters group of volatile compounds (Table 2).

3.2. Principal component analysis (PCA)

The principal component analysis (PCA) was used to determine the effect of fermentation times and drying temperature on the composition of volatile compounds in cocoa beans. The principal components (PC) were chosen according to the highest significance of fermentation time and drying temperature, as well as those with the highest explanation of the variation (Table 3, as Supplementary material). The first principal component (PC1) explained 29.88% of the total variation of the volatile compounds listed in Table 1, PC2 18.94% and PC3 11.68% (Fig. 7). The PC1 on the negative axis was highly influenced by the follow compounds: 22 (ethyl acetate), 32 (ethyl lactate), 1 (1-propanol), 2 (2-methy-1-propanol), 5 (1-pentanol) and 31 (methyl lactate) (Fig. 7a). Some of them were reported at the beginning of fermentation, such as ethyl acetate, ethyl lactate, 2-methyl-1-propanol (Fig. 7a) (Aculey et al., 2010). We observed that all these compounds were related to 2 and 4 fermentation days at all drying temperatures (Fig. 7b).

The PC1 in the positive axis grouped the compounds that can be classified into two subgroups. In the first one, we observed compounds related to the end of fermentation such as 45 (hexanoic acid), 42 (propionic acid), 47 (octanoic acid), 37 (2-phenylethyl acetate), 44 (isovaleric acid), 19 (acetophenone), 48 (nonanoic acid), and 43 (isobutyric acid) (Fig. 7a). These compounds were

Table 2
The effect of fermentation time, drying temperature and its interactions on groups of volatile compounds concentration in cocoa beans. One way analysis of variance using PROC GLM (SAS, 1989) to test for differences between treatments and Tukey's Studentized Range (HSD) test (Type I).

Treatment and interactions	*P*-value (Type I)					
	Alcohols	Aldehydes and ketones	Esters	Acids	Pyrazines	Others
Fermentation time	0.2715	0.1757	<0.0001	0.7570	0.0004	0.0296
Drying temperature	0.0081	0.5978	<0.0001	0.9932	0.4915	0.0008
Fermentation time × drying temperature	0.9858	0.9997	<0.0001	0.9998	0.5694	0.9107

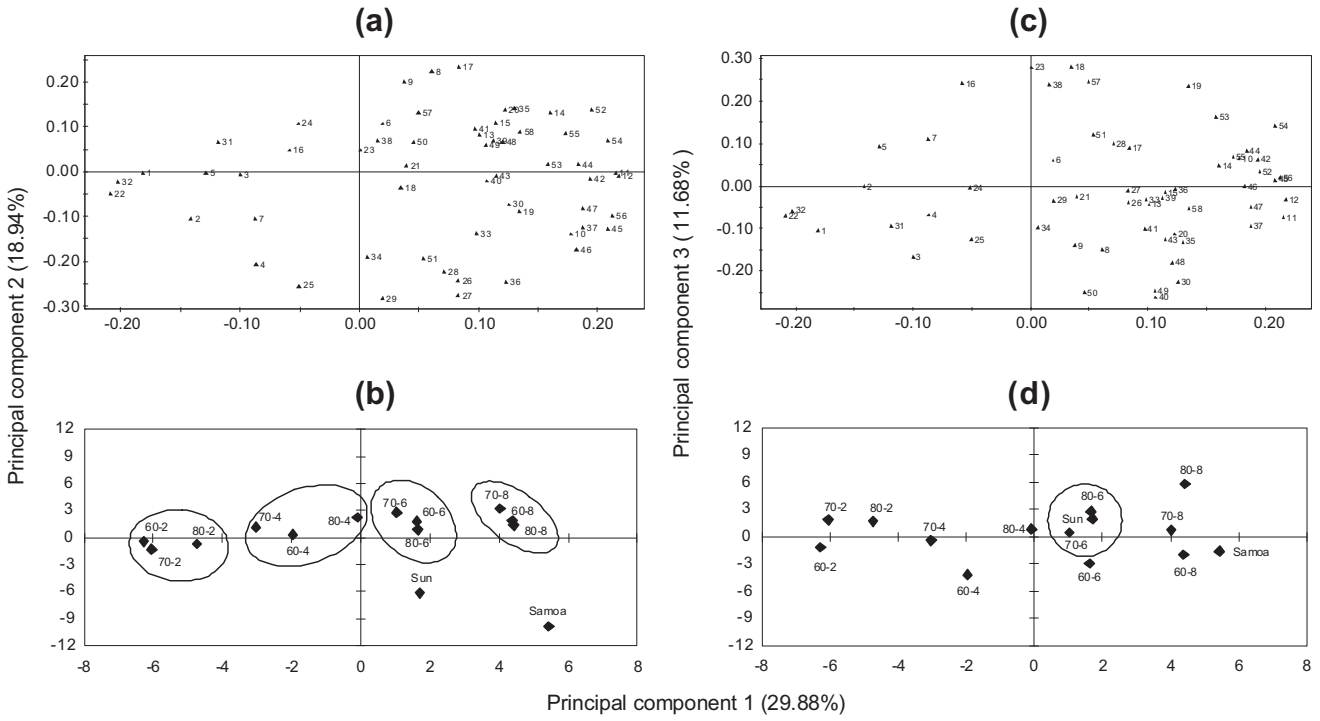

Fig. 7. Principal component analysis: Loadings plot (a) and score plot (b) of PC1 and PC2; and loadings plot (c) and score plot (d) of PC1 and PC3, from all volatile compounds in treatments. The 60, 70 and 80 are drying temperatures (°C) and the −2, 4, 6, and 8 are fermentation days; Samoa and Sun were the controls.

found at the end of the fermentation by Rodriguez-Campos et al. (2011). In the second one, we found compounds generated during the drying process (thermal process), such as 12 (phenylethyl alcohol), 11 (benzyl alcohol), 56 (2-methoxyphenol), 54 (tetramethylpyrazine), 52 (2,3-dimethylpyrazine), 10 (1-phenylethanol), 55 (2,3,5-trimethyl-6-ethylpyrazine), 14 (3-methylbutanal), 53 (trimethylpyrazine), 58 (phenol) and 30 (ethyl hexanoate), this was consistent with the compounds reported by Serra-Bonvehí and Venture (1998). These two subgroups in the positive axis were related to the treatment of eight fermentation days at all temperatures and to the Samoa control (Fig. 7a and b).

Regarding PC2, compounds with the highest weight were 17 (acetoin), 8 (2,3-butanediol), 9 (1,3-butanediol), 35 (benzyl acetate), 20 (2-phenyl-2-butenal), 15 (2,3-butanedione), 24 (ethyl formate) and 41 (acetic acid). All these compounds were grouped in the positive side and related to six fermentation days (Fig. 7a and b). While the compounds 29 (3-methyl-1-butanol acetate), 27 (ethyl 3-methylbutanoate), 25 (isobutyl acetate), 36 (ethylphenyl acetate), 26 (ethyl 2-methylbutanoate), 28 (2-penthyl acetate), 4 (3-methyl-1-butanol) and 34 (ethyl decanoate) were found on the negative axis and related to 6 fermentation days, as well as to both controls (Fig. 7a and b).

The score plot from the two first PCs (Fig. 7b), including PC1 and PC2, helped discriminate the treatments by fermentation time. Considering that some compounds produce off-flavours (such as acids (isovaleric, isobutyric, propionic), 2-methoxy phenol and phenol) the higher concentrations of these compounds after eight fermentation days suggests that is not necessary to extend the fermentation process. However, the highest concentrations of pyrazines were found after eight fermentation days, although no significant differences were observed between 8 and 6 days. In addition, compounds found after six fermentation days such as ethyl phenyl acetate, 2-penthyl acetate, acetoin, 2-phenyl-2-butenal, 2,3-butanedione, ethyl 3-methylbutanoate, ethyl 2-methylbutanoate produce desirable notes in cocoa. The acetic acid was found in high concentrations at this day of fermentation as well. However, previous reports indicate that acetic acid can be eliminated up to 70% during the roasting process (Frauendorfer & Schieberle, 2008). Given all the above, we suggest 6 days of fermentation as the optimal fermentation time. Further research is needed to evaluate the effect of acetic acid on the aromatic potential of cocoa.

In the positive axis, the PC3 grouped compounds as 18 (2-nonanone), 23 (methyl formate), 57 (2-acetyl pyrrole), 16 (2-heptanone), 38 (isoamyl benzoate), 19 (acetophenone), 53 (trimethylpyrazine), 54 (tetramethylpyrazine), 51 (dodecanoic acid), 7 (2-heptanol) and 28 (2-pentyl acetate) (Fig. 7c). These compounds were related to the Sun control and to the experimental samples obtained after six fermentation days at 70 and 80 °C (Fig. 7c and d). While the negative axis showed compounds as 40 (ethyl palmitate), 50 (undecanoic acid), 49 (decanoic acid), 30 (ethyl hexanoate), 48 (nonanoic acid), 3 (1-butanol), 9 (1,3-butanediol), 8 (2,3-butanediol), 35 (benzyl acetate), 43 (isobutyric acid),

25 (isobutyl acetate), 20 (2-phenyl 2-butenal) and 1 (1-propanol). These compounds were related to the sample of 6 fermentation days at 60 °C (Fig. 7d). The score plot from PC1 and PC3 (Fig. 7d) helped to discriminate the treatments by drying temperature. The treatments at 70 and 80 °C drying temperature were located on the positive side of PC3, while the treatments at 60 °C drying temperature were found on the negative side (Fig. 7d).

Some of these compounds were the same as the ones found by Frauendorfer and Schieberle (2008). They reported 30 aroma active compounds in unroasted and roasted Criollo cocoa such as 2-acetyl pyrrole, trimethylpyrazine, 2-heptanol, 2-pentyl acetate and isobutyric acid, acetophenone and tetramethylpyrazine. The two latter compounds were also reported to have the highest concentration in roasted cocoa (Serra-Bonvehí, 2005). Therefore, our results show that the best temperatures to obtain all these compounds were at 70 or 80 °C with six fermentation days (Fig. 7c). According to Jinap and Thien (1994), the small cocoa farmers still use sun-drying, obtaining a good quality profile of aromatic compounds. We observed that the most similar treatments to the Sun control were 80-6 and 70-6 (Fig. 7d). However, at high drying temperatures more energy is consumed and the process becomes more expensive, risking a decrease in the concentration of some desirable compounds such as tetramethylpyrazine (Hashim et al., 1999). While the concentration of undesirable compounds as 2-metoxy phenol, phenol and acid concentrations, i.e. acetic and isovaleric, can increase (Figs. 6d, 5a and c). The results of the present study showed that there were no significant differences between temperatures of 70 and 80 °C regarding alcohols, aldehydes and ketones, esters, acids and pyrazines (Figs. 2–6).

4. Conclusions

The fermentation process had a higher effect than the drying process on the profile of volatile compounds. The concentrations of some undesirable compounds occurring after 8 fermentation days suggest over-fermentation, therefore it is not necessary to extend this process for long periods. We found that 6 days of fermentation were enough to produce volatile compounds with flavour notes desirables in cocoa. The drying process at 70 and 80 °C after 6 days of fermentation resulted in a volatile compound profile similar to the one obtained by sun-drying. Therefore, we recommend as optimal conditions 6 days of fermentation followed by drying at 70 °C, which represent a low cost while avoiding the production of compounds with off-flavour notes.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.foodchem.2011.10.078.

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