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Chemical composition and thermal characterization of selected Philippine cacao (*Theobroma cacao* L.) and tablea

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ABSTRACT

Cacao (*Theobroma cacao* L.) is a high-value crop grown in tropical countries where it is processed to make products like chocolate. In the Philippines, cacao is also used to produce a traditional product from cacao liquor called tablea. In the production of tablea, it is necessary to investigate the composition and physicochemical properties to evaluate its nutritional attributes, and product quality. Hence, this study investigated the composition and thermal properties of cacao and Philippine tablea from three different locations through proximate composition analysis, gas chromatography-mass spectrometry (GC-MS), Fourier transform infrared spectroscopy (FTIR), differential scanning calorimetry (DSC), and thermogravimetric analysis (TGA). Results showed a decrease in moisture from cacao to tablea due to roasting. GC-MS analysis revealed a total of 27 compounds from all the samples analyzed. The presence of polysaccharides, lipids, proteins, and phenolics was evident in all mid-FTIR spectra samples. The melting profile indicated that cocoa butter polymorph form V was the native structure of the cocoa butter in all samples, which is ideal for cacao-derived products. Additionally, repeated rapid heating and cooling of the cacao and tablea samples favored the formation of cocoa butter polymorph forms of lower stability. The TGA profile of cacao and tablea revealed the temperature ranges attributable to the degradation of polysaccharides, cocoa butter, and proteins. The DSC and TGA thermograms of cacao and tablea counterparts indicate similar phase transitions and thermal degradation events. This study provided insights into the composition and thermal properties of cacao and Philippine tablea, which can be used as a baseline for quality and product development in the country.

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INTRODUCTION

Cacao (*Theobroma cacao* L.) is a valuable crop grown as an income source for many farmers in developing countries near the equator (Department of Agriculture 2016). Global sales volume of cacao-derived products is expected to increase to 7.61 million tons in 2023 from 7.56 million tons in 2022

KEYWORDS

Theobroma cacao, Philippine tablea, chemical composition, thermal analysis, thermal properties, fatty acid polymorph

(International Cacao Organization 2023). The Philippines produced 9.34 metric tons of cacao in 2020, and the demand for cacao is seen to increase yearly (Department of Agriculture - Bureau of Argicultural Research 2022). Industry analysis revealed that the Philippine Cacao trade is comprised chiefly of small-scale chocolate manufacturers and tablea makers (Department of Agriculture - Bureau of Argicultural Research 2022; Department of Trade and Industry 2017). Tablea is a solidified cacao mass from cocoa liquor, which serves as an ingredient in *Champorado*, a chocolate-flavored rice porridge; and *Sikwate*, a local chocolate drink (Vera 2018). Making tablea starts with obtaining the beans and fermenting them to get a particular flavor profile. Drying and roasting of the beans then follows. From there, the roasted cacao beans are winnowed to remove the shell that covers the nib. The nib is then ground to a paste which is called cocoa liquor. After, the cocoa liquor is molded into shape, packaged, and sold as tablea (Vera 2018; Barrion, Hurtada, and Amalin 2016; Calica and Mari San Pedro 2023).

In food products, product quality depends on composition and processing history (Ostrowska-Ligęza et al. 2019; Şekeroğlu and Kaya 2021). Tablea is made mainly of fatty cocoa butter. Other components, such as carbohydrates and proteins are suspended in the cocoa butter matrix (Barrion, Hurtada, and Amalin 2016). The triacylglycerol (TAG) profile of cacao crystallizes in six (6) known polymorphic forms (form I- VI) of cocoa butter that confer different thermodynamic stabilities, appearances, and physical properties (Ostrowska-Ligęza et al. 2019; Beckett 2008; Becu et al. 2011; Wille and Lutton 1966; Marcel and Dezena 2021). The polymorphic structure greatly influences the viscosity, melting behavior, and flavor of the final product (Melo et al. 2020). Therefore, it is an excellent quality parameter for tablea (Tisoncik 2010; Engeseth and Pangan 2018).

Quick and sensitive techniques for food analysis are valuable tools in assessing the quality of the final food product. Analyses such as GC-MS, DSC, and TGA can give insights into the composition and thermal properties of cacao-derived products, which are important since several factors that contribute to product quality, such as hardness, appearance, gloss, and flavor release, among others, are dependent on structure and temperature (Ostrowska-Ligęza et al. 2019; Beckett 2008; Wille and Lutton 1966; Tisoncik 2010; Engeseth and Pangan 2018; Afoakwa 2016). Additionally, manufacturing processes may affect the structural, chemical, and thermal properties of the final product. Several studies have investigated the DSC melting profile and TGA curve of cacao beans, cocoa butter, and chocolate, and their thermal properties are understood (Ostrowska-Ligęza et al. 2019; Melo et al. 2020; M. R. Rojas et al. 2020; Sandoval et al. 2019; Materazzi et al. 2014). However, the same cannot be said for Philippine tablea. To the best of our knowledge, the composition of Philippine tablea investigated via GC-MS and FTIR, and its thermal properties via DSC and TGA have not been reported to date.

This present work was primarily focused on the assessment of the composition and thermal properties of cacao beans and Philippine tablea collected from three (3) locations in the Philippines namely, Quezon, Bohol, and Davao.

MATERIALS AND METHODS

Sample collection and processing

Three (3) tablea products, one from Bohol, Davao, and Quezon, were used in this study. Table 1 shows pertinent sample information. Information on food processing such as fermentation, drying, roasting, winnowing, and grinding were requested from each tablea maker. All tablea manufacturers obtained dried and fermented cacao beans from a market source. The cacao beans used in this study are the same cacao beans used in making the tablea. Most market-sourced cacao beans come from farms that cultivate multiple varieties (Millena et al. 2023). Use of a single variety of cacao is not a common practice of local tablea makers. Nonetheless, it is pertinent to acknowledge that approximately 70% of the cacao yield in the Philippines is attributed to the Trinitario variety (Department of Agriculture - Bureau of Argicultural Research 2022). The manufacturers then performed the downstream processing following the steps in tablea manufacturing as specified by the Code of Practice for Philippine Tablea (PNS/BAFPS 88:2012) ("Bureau of Philippine Standards" 2012). For the Bohol sample, roasting was traditionally done in a wok using wood as feedstock for the fire. Constant stirring was performed for even roasting, and the process lasted approximately 40 minutes. On the other hand, the Davao and Quezon samples used roasters fueled by gas. Specific information on roasting parameters and practices was withheld at the behest of the manufacturer. As such, the variety of the cacao used and the specific parameters of roasting of the Bohol and Davao samples were limitations of the study.

Table 1. Information on the different cacao and tablea samples.

Code	Origin	Sample	Cacao farm location
BC	Bohol	cacao	Jagna, Bohol
BT		tablea	
DC	Davao	cacao	Davao del Sur
DT		tablea	
QC	Quezon	cacao	Candelaria, Quezon
QT		tablea	

Determination of the proximate composition of the cacao and tablea samples

Approximately 400 grams of tablea and dried peeled cacao from each sample were submitted to the Analytical Services Laboratory of the Institute of Plant Breeding at the University of the Philippines Los Baños for analyses. Protocol for the proximate composition analysis for the percent moisture, crude fat, protein, carbohydrate, fiber, and ash content are explained below.

Percent moisture was measured by calculating the weight difference of the homogenized sample after incubation in an oven at 50°C for 48 hours. Crude fat was measured by first obtaining the fat component via Soxhlet fat extraction using petroleum ether as solvent. The samples were then refluxed for eight (8) hours, and the exact weight of the residue was determined after desiccation. Protein content was determined using the macro Kjeldahl digest procedure. Crude fiber was measured by subjecting the defatted sample to reflux conditions with sulfuric acid. Subsequently, the samples were neutralized and subjected to reflux conditions in sodium hydroxide and then washed with hot distilled water. The samples were then dried overnight at 105°C and subsequently ignited in an oven at 650°C for eight (8) hours. After, the exact weight of the residue was obtained, percent ash content was determined. The above-mentioned analyses were performed in three (3) replicates.

Gas chromatography-mass spectrometry (GC-MS) with electron ionization (EI)

Ground dried cacao seeds and their respective tablea samples (~3.0 g) were soaked in 20 mL dichloromethane (DCM) for 72 hours. Preliminary trials of incubation or maceration of these samples were optimized to ensure best results in terms of the total ion chromatograms produced. Extracts were filtered, then concentrated over nitrogen gas and reconstituted with 0.5 mL DCM. These were then filtered using a 13 mm polytetrafluoroethylene (PTFE) 0.45 µm Whatman syringe filter.

After sample preparation, GC-EI-MS (Agilent GC MS7890B, equipped with a HP-5 ms (5% phenyl methylsiloxane) Ultra Inert column (30 m × 250 mm × 0.25 mm) with ultrapure helium gas as the mobile phase) experiments were performed using a method previously published (Tan et al. 2019). The substantiated phytochemicals of the extracts were established through retention indices (RI), whenever possible, and structural categories by means of NIST Archive.

FT-IR analysis of the cacao and tablea samples

The ground cacao and tablea samples were analyzed in a Fourier Transform Infrared spectrophotometer (FTIR, Shimadzu Corp., Kyoto, Japan) coupled to an ATR accessory of QATR-S with a diamond reflection crystal. The spectra were acquired in the 4000–600 cm^{-1} range, with 4 cm^{-1} resolution, 64 scans, and were subjected to background subtraction (atmosphere spectra) and ATR correction using IRsolution Ver. 1.20 software (Shimadzu Corp., Kyoto, Japan).

Differential scanning calorimetry

Before DSC measurements, the tablea and dried cacao bean samples were ground using a mortar and pestle. Subsequently, the ground powder was filtered using a 60-mesh sieve to obtain particle sizes of less than 250 microns. Then, the samples were analyzed in a differential scanning calorimeter (TA Instruments, DSC 25). Approximately 5.0 mg of the sample was loaded into hermetically sealed aluminum pans and analyzed subsequently. The scan was run under a nitrogen atmosphere at an airflow rate of 20 mL/min. The DSC protocol is summarized in Table 2. Specifically, the DSC protocol for each sample can be described by two heating and cooling cycles followed by a final heating run. An empty hermetically sealed aluminum pan was used as a reference. The DSC experiments were conducted in triplicates.

Table 2: DSC protocol for the cacao and tablea samples.

Step	Cycle	Process
0		Start of DSC run
1		Let the sample sit at the standby temperature (10°C)
2	1	Ramp temperature from -5°C to 60°C (scan rate = 5°C/min.)
3		Ramp temperature from 60°C to -5°C (scan rate = 5°C/min.)
4		Maintain isothermal conditions at -5°C for 10 mins.
5	2	Ramp temperature from -5°C to 60°C (scan rate = 5°C/min.)
6		Ramp temperature from 60°C to -5°C (scan rate = 5°C/min.)
7		Maintain isothermal conditions at -5°C for 10 mins.
8	3	Ramp temperature from -5°C to 60°C (scan rate = 10°C/min.)
9		Jump temperature to 25°C
		End of DSC run

Thermogravimetric analysis

The change in mass of cacao beans and tablea samples with respect to temperature was investigated using a thermogravimetric analyzer (TA Instruments, TGA 55). The samples were prepared into a uniform powder using the same procedure described in the DSC protocol. The weight of the samples loaded into the aluminum oxide crucibles varied in the range of 5.0 to 20.0 mg. The TGA run was conducted under a nitrogen atmosphere from 30°C to 700°C at a scan rate of 10°C/min. The TGA runs were performed in triplicates, and the change in the relative mass was investigated.

Statistical Analysis

Data produced from the proximate composition analysis, DSC, and TGA were analyzed via paired t-test to determine whether a statistical difference exists between the parameters measured from the cacao and tablea samples using XLSTAT software (Data Analysis and Statistical Solution for Microsoft Excel, Addinsoft, Paris, France 2017). Additionally, one-way ANOVA with Tukey's test as post-hoc analysis ($\alpha = 0.05\%$) were performed using online freeware ASTATSA (https://astatsa.com/OneWay_Anova_with_TukeyHSD/) to compare the proximate composition of the samples across different locations.

RESULTS AND DISCUSSION

Chemical Composition of the Cacao and Tablea Samples

Table 3 shows the proximate composition of the cacao and tablea samples. The moisture of the cacao samples ranged from 3.68% to 4.44%, which was lower compared to the moisture content of cacao beans from Ecuador, Peru, and Venezuela, which was 5.70%, 5.50%, and 6.22%, respectively (Ostrowska-Ligęza et al. 2021; Sandoval et al. 2019). On the other hand, the moisture content of the tablea samples in this study ranged from 1.46% to 1.87%, within the range reported by a previous study that measured the moisture content of tablea samples to be from 0.29% to 1.90% (Barrion, Hurtada, and Amalin 2016). Overall, the cacao and tablea samples measured in this study had moisture content within the allowable limit of 7.50% set by the Philippine National Standard for tablea ("Bureau of Philippine Standards" 2012). However, it is pertinent to point that this maximum value only pertained to the storage of cacao beans. In the current code, there is no maximum moisture value specific for the final tablea product. A comparable standard for tablea is the 2% moisture content maximum value for chocolate bars required by Indonesian products (Ratrina and Sitorus 2022; Standar Nasional Indonesia 2009). Having a similar standard for tablea would be beneficial to standardize and improve the shelf life and quality of Philippine tablea.

It is important to note that all samples showed a significant decrease in moisture from cacao to tablea. The average decrease in moisture content was 1.81%, 2.23%, and 2.59% for Bohol, Davao, and Quezon, respectively. This decrease was due to the roasting process, which develops flavor and makes the shell easier to crack. Ensuring the correct moisture level prevents the growth of molds which prolongs shelf-life. Furthermore, it also ceases the remaining microbial and enzymatic activities left over from fermentation (Thompson SS, Miller KB, Lopez AS, n.d.; Ackah and Dompey 2021).

Crude fiber is the indigestible organic component of food which is essential for maintaining a healthy digestive system (Barrion, Hurtada, and Amalin 2016). Crude fiber from the cacao samples in this study ranged from 5.67% to 9.00%. The crude fiber content of tablea samples ranged from 3.67% to 4.67%. Fat was a significant component of cacao and tablea. The crude fat content was found to be the major component of the cacao and

tablea samples. Both saturated and unsaturated fatty acids mainly comprise the crude fat content which is consistent with the results of the GC-MS data in the subsequent section. For crude protein, the relative amount in tablea was higher compared to its cacao counterpart across the three locations. The variation in the crude protein content in the cacao and tablea samples may be attributed to the amount of nitrogen in the soil where the cacao was planted, as well as the cultivar of the cacao used (Melo et al. 2020). Additionally, variable roasting practices from each manufacturer may also contribute to the difference in crude protein content since roasting primarily influences protein composition through the Maillard reaction (M. Rojas et al. 2022). Lastly, ash, an inorganic substance that remains after combustion of organic materials, was measured to assess the mineral content found in the ingredients of food products. In terms of composition, ash was found to be a minor constituent in the samples at ranges between 3.59% and 4.48% for cacao, and 3.30% and 4.70% for tablea (Ratrina and Sitorus 2022).

Comparing the proximate analysis of the cacao and tablea samples from the 3 different locations, some differences were observed. Cacao from Quezon had a significantly higher moisture content while cacao from Bohol had a significantly lower crude fat content. For the tablea samples, tablea from Davao has a significantly lower crude fat and higher ash content. Furthermore, all 3 tablea samples had significantly different total carbohydrates. Although Davao and Quezon tablea makers use gas-fueled roasters, they may have used different roasting parameters which led to different outcomes in total carbohydrate content. According to the Philippine national standard Code of Practice for Philippine Tablea, the tablea makers are given liberty in choosing the roasting parameters for their products. This means that the difference in the variety of cacao used and the process of roasting may be possible reasons for the differences observed.

Table 3. Results of the proximate composition analysis of the cacao and tablea samples shown as % by mass.

Sample	Moisture content, %	Crude Fat, %	Crude Fiber, %	Crude Protein, %	Total Ash, %	Total Carbohydrates, %
BC	3.68 ± 0.12[a]	43.64 ± 0.85 [a,b]	9.00 ± 1.00	22.28 ± 0.17 [a]	3.59 ± 0.02 [a]	17.81 ± 1.33 [a]
BT	1.87 ± 0.34	50.17 ± 1.31	4.67 ± 2.08	30.74 ± 0.69	3.30 ± 0.07	9.26 ± 2.50 [b]
DC	3.69 ± 0.07 [a]	47.10 ± 1.22	6.00 ± 1.00	23.56 ± 0.22 [a]	4.48 ± 0.56	15.17 ± 1.69
DT	1.46 ± 0.23	45.55 ± 0.50 [b]	3.67 ± 1.53	29.13 ± 1.00	4.70 ± 0.07 [b]	15.49 ± 1.91 [b]
QC	4.44 ± 0.10 [a,b]	46.58 ± 0.41 [a]	5.67 ± 2.08	20.67 ± 0.92 [a]	3.70 ± 0.41	18.94 ± 2.35 [a]
QT	1.85 ± 0.04	50.96 ± 0.08	4.33 ± 0.58	37.15 ± 0.30 [b]	3.66 ± 0.09	2.05 ± 0.66 [b]

[a] significant difference (α=0.05) when comparing the cacao sample to its tablea counterpart. Dependent t-tests were done between cacao and tablea of the same location.
[b] significant difference (α=0.05) when comparing the proximate composition of the samples across different locations.

Overall, this study found a uniform increase in the relative amount of protein, decrease in moisture content, and similar crude fiber content when comparing the proximate composition of cacao and tablea. This may be attributable to the roasting process. Although the manufacturers employ different strategies in the roasting process, Rojas, et al. (2022) reported that roasting temperature generally ranges from 110 °C to 160 °C. Previous thermogravimetric studies of cacao samples suggest that macromolecules degrade at different temperature ranges, with moisture loss specifically happening between 30 °C and 120 °C (Melo et al. 2020; Sandoval et al. 2019). Additionally, simultaneous pyrolysis of high molecular weight polysaccharides is observed at between 120 °C and 180 °C (Materazzi et al. 2014), while protein decomposition happens from 455 °C and 520 °C (Sandoval et al. 2019). As such, it can be deduced that the temperature of roasting was sufficient for moisture loss but not for the degradation of fiber and proteins. The elevated relative protein content was attributed to the degradation of other components. Non-uniform changes were observed for other components. Specifically, crude fat increased from cacao to tablea in all the trials except for the Davao specimens. As for total carbohydrates, all samples showed a decrease in its content from cacao to tablea except for the Davao samples. There was a decrease in total ash content for the Bohol samples from cacao to tablea for total ash, but this was not seen in the other samples. The nonuniform changes for the mentioned components may be explained by differences in post-harvest processing, especially the manufacturing techniques used by cacao manufacturers (M. Rojas et al. 2022).

Gas chromatography-mass spectrometry (GC-MS) with electron ionization (EI)

Cacao and tablea DCM-soaked extracts were evaluated via GCMS to assess their chemical composition further. Results revealed a total of 27 compounds in all samples which are summarized in Table 4. Different compound groups were found in the cacao and tablea samples in this study such as fatty acids, phytosterols, ketones, carbinols, alkaloids, phenylaldehydes, an allocholate derivative, and an isophthalate. Additionally, most compounds detected in the cacao and tablea samples were fatty acids and fatty acid esters. These results are consistent with the proximate composition analysis of this study. Most of the fatty acids in cacao are palmitic acid (C16:0), oleic acid (C18:1), and stearic acid (C18:0). These were detected in the samples as fatty acid esters and their fatty acid ester counterparts. These fatty acids contribute significantly to the polymorphism and melting profile of the cacao and tablea samples, which are discussed in section 3.4 (Beckett 2008). Ethyl palmitate was found in BC, DT, QC. And QT.

Table 4. Composition of DSC-soaked extracts of cacao and tablea. Complete details on the retention times and indices can be found on the Supplementary Information.

	Compound	Functionality	% Peak area					
			BC	BT	DC	DT	QC	QT
1	Ethyl stearate	fatty acid ester	8.10			5.3	2.8	1.1
2	Ethyl oleate	fatty acid ester	5.60				7.8	
3	Ethyl-9,12-octadecadienoate	fatty acid ester	3.90				5.3	
4	Ethyl ester tetradecanoic acid	fatty acid ester				0.7		
5	Ethyl palmitate	fatty acid methyl ester	65.80			10.4	3.8	6.2
6	Methyl palmitate	fatty acid methyl ester		6.60		2.0		1.7
7	Methyl stearate	fatty acid methyl ester		5.60				1.7
8	methyl-10-octadecenoate	fatty acid methyl ester						1.9
9	Stearic acid	saturated fatty acid		31.50	32.0	10.2		4.2
10	Palmitic acid	saturated fatty acid		22.80	26.5	18.6		16.6
11	trans-δ9-Octadecenoic acid	unsaturated fatty acid			27.0			
12	Oleic acid	unsaturated fatty acid			1.9			45.0
13	γ-Tocopherol	tocopherol	3.00	2.10		3.6	5.4	1.3
14	Stigmasterol	phytosterol	5.70	1.60	1.6	3.9	4.5	2.3
15	γ-Sitosterol	phytosterol	4.70	7.00				
16	β-Sitosterol	phytosterol			1.5	10.1	4.6	4.3
17	Benzophenone	diarylketone				0.5		
18	2-Heptadecanone	ketone		4.60		18.6		0.9
19	2-Nonadecanone	ketone		2.40		3.2		1.4
20	α,α-diphenyl-benzenemethanol	carbinol		6.80				10.7
21	Ethyl iso-allocholate	allocholate derivative	3.20					
22	Caffeine	purine, methylxanthine alkaloid		9.20	4.9	21.2	62.8	0.6
23	Triphenylmethane	triarylmethane				5.9		
24	2,2'-Methylene-bis(6-tert-butyl)-para-cresol	cresol derivative			1.9			
25	Bis(2-ethylhexyl) isophthalate	isophthalate			2.6		3.0	
26	5-Methyl-2-phenyl-2-hexenal	phenylacetaldehydes				1.0		
27	Hexahydro-3-(2-methylpropyl)-pyrrolo[1,2-a]pyrazine-1,4-dione	diverse functional groups				2.2		

For the tablea samples, palmitic acid, stearic acid, and methyl palmitate were acquired in all three (3) extracts. Methyl stearate was found only in BT and QT. Ethyl palmitate and ethyl stearate were seen in QT and DT, whereas methyl-10-octadecenoate was only found in QT, and ethyl ester tetradecanoic acid was detected in DT exclusively. Oleic acid, a monounsaturated omega-9 fatty acid, was only detected in QT. Whereas monounsaturated fatty acids (MUFAs), oleic acid, and trans-δ9-octadecenoic acid were detected in DC only. The cacao and tablea samples in this study were seen to be comprised of a diverse set of fatty acids. These assemble into TAGs, and the diversity of fatty acid arrangements causes polymorphism in its structure (Beckett 2008; Melo et al. 2020; Ostrowska-Ligęza et al. 2021).

Phytosterols such as γ-tocopherol, stigmasterol, and β-sitosterol were detected in the different samples. γ-Tocopherol, which was found in QC, BC, BT, DT, and QT, provided distinctive fragmentation peaks in the spectrum associated with the molecule. γ-Tocopherol is a major isoform of vitamin E and has been shown to have antioxidant activities, showing high activity in trapping lipophilic electrophiles and reactive nitrogen species (Wagner, Kamal-Eldin, and Elmadfa 2004). Stigmasterol was found in all samples, while β-sitosterol was detected in the Davao and Quezon samples only. Stigmasterol has been reported to have several pharmacological effects such as anticancer, anti-osteoarthritis, anti-inflammatory, and anti-diabetic properties among others (Bakrim et al. 2022). While β-sitosterol has anxiolytic, analgesic, immunomodulatory, and anti-diabetic activities among others (Babu and Jayaraman 2020). Caffeine was found in the cacao and tablea samples except BC. It is a stimulant, and the most widely consumed psychoactive substance (Hall et al. 2015). The fragmentation patterns generated from the five extracts of caffeine showed characteristic spectra for this molecule.

Ketones such as 2-heptadecanone and 2-nonadecanone, which are indicative of roasting, were detected in all tablea samples, but not in the cacao samples. Ketones and aldehydes are formed during cacao bean roasting as these are the products of Strecker degradation of amino acids (Calva-Estrada et al. 2020). Other compounds from different compound classes were also seen in the cacao samples. The phthalate ester, bis(2-ethylhexyl) isophthalate, was established in QC and DC. It is a common plasticizer and environmental pollutant known to contaminate water and soil (Lo, Wang, and Wu 2014). The carbinol, α,α-diphenyl-benzenemethanol was seen in both BT and QT. 5-Methyl-2-phenyl-2-hexenal ($C_{13}H_{16}O$) was solely displayed in DT. This compound imparts the characteristic cocoa fragrance and is often associated with mocha undertones in cocoa-derived products (Chen and Robbins 2000; Ramli et al. 2006). A minimal amount of benzophenone, a flavoring agent, was also displayed in DT.

Among cacao samples, more compounds were found in DC and QC than in BC. As for tablea, it was DT, QT, and BT in decreasing order of the number of compounds found. These differences may be attributable to geographical location and the variety of cacao used. Additionally, further variability in the composition profile of the samples may be caused by stages in its processing such as fermentation and roasting, which subject the samples to enzymatic breakdown and high temperatures that produce compound by-products. Differences in the conditions of such processes may alter the types of compounds produced from such processes (Calva-Estrada et al. 2020; Ascrizzi et al. 2017; Santander Muñoz et al. 2020).

FT-IR analysis of the cacao and tablea samples

The spectral characteristics of both cocoa beans and tablea samples were obtained by mid- FTIR analysis, and these findings are shown in Figure 1. All samples include functionalities such as -OH stretching vibration (~3300 cm^{-1}) found in phenolics and polysaccharides, C-H stretch in CH_2 and CH_3 groups (~2920 and ~2850 cm^{-1}) in lipids, C=O stretch (~1750 cm^{-1}) in carboxylic acids, aldehydes and ketones, C=C valence deformation (~1650 cm^{-1}) in fatty acids, amide I (~1630 cm^{-1}) and amide II (~1550 cm^{-1}) in proteins, and aromatic skeletal vibrations (~1520 cm^{-1}) mainly found in phenolics. These same functional groups were also detected in both Ecuadorian cocoa shells and beans (Grillo et al. 2019). Hence,

no noticeable differences occurred in the mid-FTIR spectra of all the analyzed cacao bean and tablea samples.

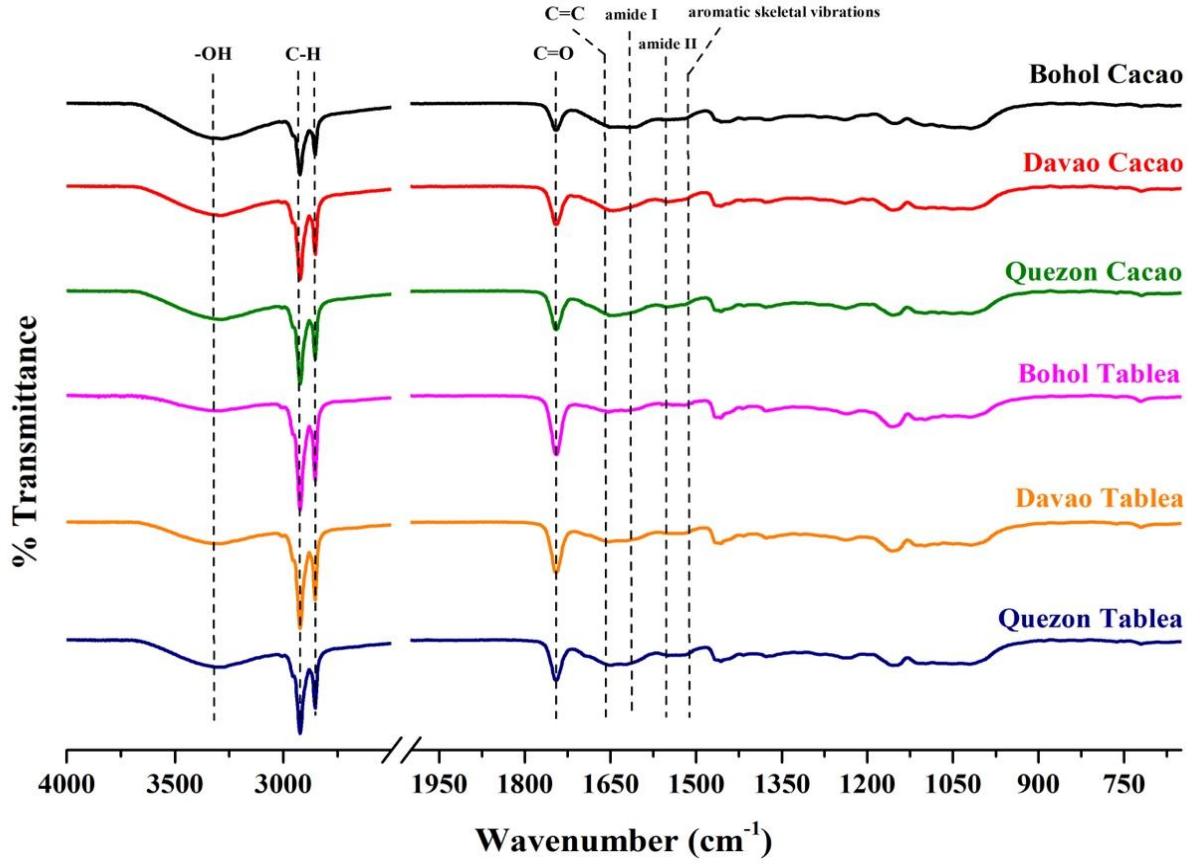

Figure 1: FTIR spectra of the cacao and tablea samples.

Melting and cooling profile of cacao and tablea

The DSC melting profile of all samples on the first heating run is shown in Figure 2. All cacao and tablea samples showed a single endothermic peak temperature (T_{peak}) from 32.27 °C to 33.65°C, which represents the melting of the native polymorph structure of cocoa butter in the samples (Beckett 2008; Spigno, Pagella, and De Faveri 2001; Ghazani and Marangoni 2021; Afoakwa et al. 2009). The native polymorph structure of the cocoa butter observed in both the cacao and tablea samples was form V, which has a T_{peak} between 30.00 °C and 34.50 °C (Beckett 2008; Ghazani and Marangoni 2021; Hajiyeva and Shamilova 2021; Marcel and Dezena 2021). This suggests that the roasting and grinding process in making tablea does not have a detrimental effect on the TAG content of cocoa butter, and form V is restored after the solidification of the cacao liquor upon molding to form solid tablea. Form V is the ideal polymorph structure for cacao-derived products (Dezena 2021; Sandoval et al. 2019) as this form has sensorial and physical properties ideal for consumption such as having a glossy appearance, good snap when breaking, and enhanced shelf life (Ostrowska-Ligęza et al. 2021; Rousseau and Sonwai 2008; Ostrowska-Ligeza et al. 2023). In chocolate products, a process called tempering is performed prior to solidification upon molding. Tempering is done to achieve an even crystallization of the Form V polymorph (Beckett 2008). However, this is not practiced in the manufacturing of tablea. Additionally, tempering is also not specified in the molding practices of the Code of Practice for Philippine Tablea, resulting in the inconsistencies in the appearance of the product. Despite finding Form V in all tablea samples in this study, there is still a need for a detailed Code to improve the quality of the tablea products produced by local tablea makers.

Thermal parameters of melting such as T_{peak}, onset temperature (T_{onset}), endset temperature (T_{endset}), melting index (T_{index}), and enthalpy of the cacao and tablea samples are shown in Table 5. The T_{onset} and T_{endset} reveal the point at which the melting of a specific crystal structure begins and ends, respectively. Then, T_{index} is calculated as the difference between T_{endset} and T_{onset}, which reflects the melting peak width. The T_{index} of the cacao and tablea samples ranged from 6.06-8.44°C. All values of T_{onset}, T_{endset} , and T_{index} for the tablea samples are appropriate because a narrow and sharp melting peak below the body temperature is ideal since it confers a quick-melting effect and smooth mouth-feel (Clercq et al. 2014; Biswas et al. 2017). This is ideal for solid applications of tablea, such as tablea shavings as a topping to confectioneries and pastries.

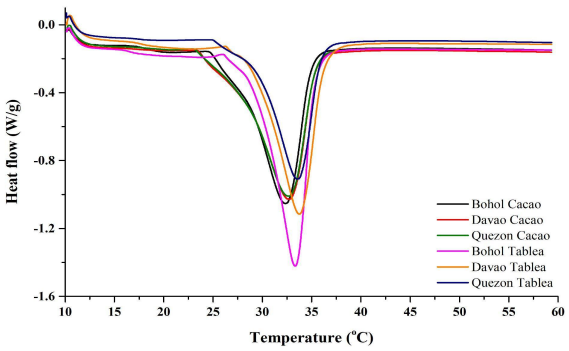

Figure 2: DSC thermogram of the 1st heating run of BC, BT, DC, DT, QC, and QT.

Melting enthalpy is the energy required to break the crystalline structure of the cocoa butter as it transforms from solid to liquid. The cacao and tablea samples recorded melting enthalpies ranging from 47.48 J/g to 65.33 J/g. There was a significant change in the enthalpy measured between the cacao and tablea

samples from Davao and Quezon. However, no significant change was observed for the Bohol samples. The varying observation in the melting enthalpy may be attributed to the multicomponent nature of the samples (Ioannidi et al. 2021). The T_{endset}, and T_{index} values obtained from the cacao and tablea samples originating from the same locality exhibit no significant differences.

In the DSC protocol, two heating and cooling cycles were performed followed by a third melting run. This is to simulate temperature fluctuations in uncontrolled storage conditions. The thermograms of all six cacao and tablea samples showed similar phase transitions. A representative DSC thermogram is shown in Figure 3. The first heating cycle reveals the melting profile of the pristine cacao and tablea sample while at the same time erasing its crystal memory for the subsequent cycles. The cacao and tablea samples recrystallized from 10.89 °C to 12.11 °C during cooling corresponding to the formation of the metastable polymorph, form I (Beckett 2008; Ghazani and Marangoni 2021; Bresson et al. 2011). The samples were then incubated at isothermal conditions (-5°C) for ten minutes before proceeding. On the second heating cycle, the cacao and tablea samples showed an endothermic peak, this time, ranging from 17.64 °C to 19.40 °C. This showed the rapid decomposition of form I into the more stable structure– form II. The run then proceeded with the second cooling cycle which appears similar to the first cooling cycle. The samples were then incubated at isothermal conditions (-5°C) for ten minutes. Lastly, a third heating run was performed, which revealed the melting of form II from 18.40 °C to 20.46°C. The third heating run shows an increase in the T_{peak} of form II. This is the result of thermal lag since the run was performed at 10°C/min– twice the scan rate of the previous runs (5°C/min) (M. R. Rojas et al. 2020; Gaisford 2008).

Table 5. Mean values of the melting parameters of the cacao and tablea samples for the first melting cycle.

Sample	Melting parameters				
	T_{Peak} (°C)	T_{onset} (°C)	T_{endset} (°C)	T_{index} (°C)	Enthalpy (J/g)
BC	32.44±0.17	27.32±0.05*	35.35±0.22	8.03±0.19	59.97±1.75
BT	33.05±0.16	29.08±0.45	35.14±0.39	6.06±0.07	65.33±3.79
DC	32.57±0.11	27.02±0.01*	35.32±0.23	8.29±0.23	61.99±0.45*
DT	33.11±0.72	28.94±0.25	35.65±0.42	6.72±0.48	57.44±1.49
QC	32.58±0.29	27.04±0.21*	35.47±0.35	8.44±0.19	63.93±0.94*
QT	33.51±0.16	29.09±0.10	35.88±0.13	6.79±0.04	47.48±4.42

**significant difference (α=0.05) when comparing the cacao sample to its tablea counterpart. Dependent t-tests were done between cacao and tablea of the same locality.*

The repeated heating and cooling runs performed on the cacao and tablea samples showed that once form V is melted, it is not regained with rapid heating and cooling rates. Instead, more unstable polymorphs are formed such as form I and form II. Additionally, the thermograms of the first and second cooling were similar indicating that from -5 °C to 60 °C, there was no degradation of the cocoa butter and that the melting and cooling of cocoa butter is reversible. Furthermore, fat bloom was also observed, which is the transformation of unstable polymorphs to more stable conformations. Fat bloom manifests as large white crystals on the surface of cacao-derived products. Although the food product is safe for consumption, the appearance and optimum sensorial characteristics of the cocoa butter make it less desirable (Lonchampt and Hartel 2004; Bricknell and Hartel 1998). With this, it is seen that temperature fluctuations in improper storage conditions can melt form V and erase thermal memory, which damages tablea products. Similarly, temperature swings may favor the formation of unstable polymorph forms which decreases the quality and overall appeal of the product, highlighting the need for adequate temperature control both in manufacturing and storage to preserve the structure of form V.(Ostrowska-Ligęza et al. 2019; Melo et al. 2020; Ostrowska-Ligęza et al. 2021).

Thermogravimetric analysis

The TGA profile of the cacao and tablea samples from Bohol, Davao, and Quezon are shown in Figure 4. Five (5) mass loss steps were observed in the TGA curves, which are attributable to the thermal degradation of its major components. The first mass loss step was observed from 30°C to 120 °C which is related to the evaporation of loosely bound water molecules (Melo et al. 2020; Sandoval et al. 2019). The second step, from 120°C to 280°C is attributed to the simultaneous pyrolysis of high molecular weight polysaccharides (Materazzi et al. 2014). The third (from 280 °C to 385 °C) and fourth (from 385 °C to 455 °C) steps were related to the release of cocoa liquor and the thermal decomposition of fat (Ostrowska-Ligęza et al. 2019; Melo et al. 2020; Ostrowska-Ligęza et al. 2021; Dippong et al. 2021). Lastly, the fifth step was observed from 455°C to 520°C, which is attributed to further decomposition of organic compounds and decomposition of proteins (Sandoval et al. 2019). Residue collected at the end of the TGA run is attributed to ash which is made of high stability inorganic components (Ostrowska-Ligęza et al. 2021).

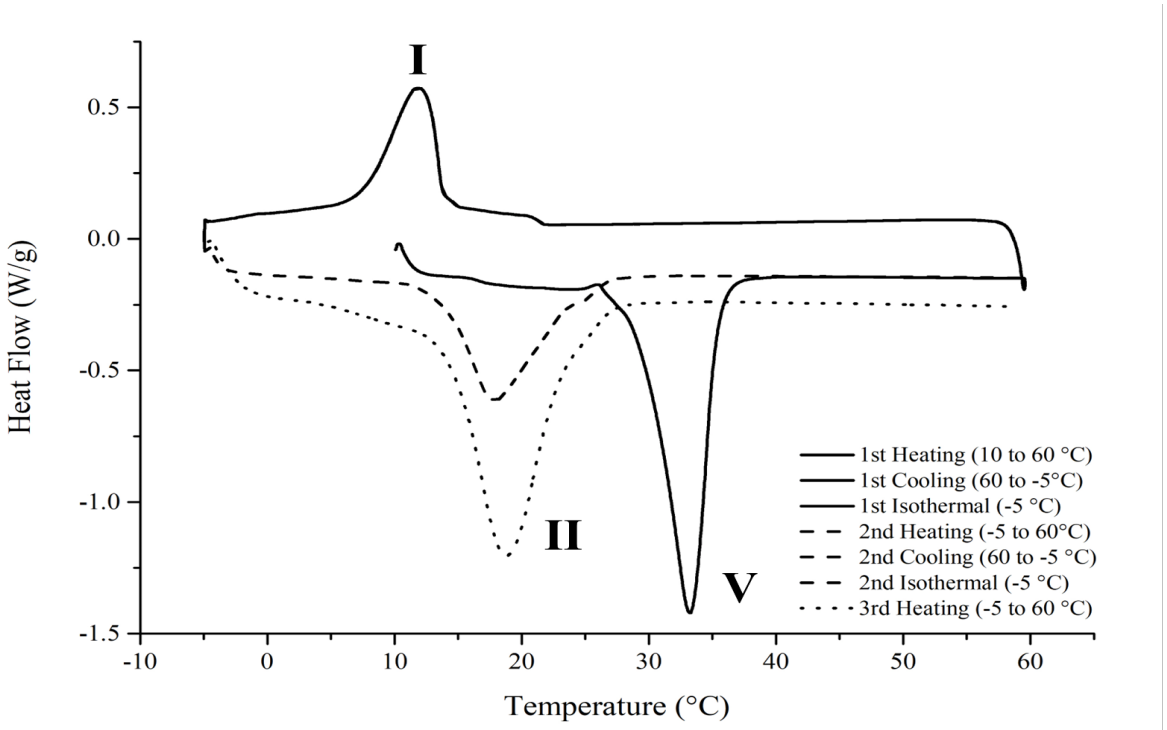

Figure 3: Representative DSC thermogram of all six cacao and tablea samples throughout the DSC protocol. The thermogram used is from BC.

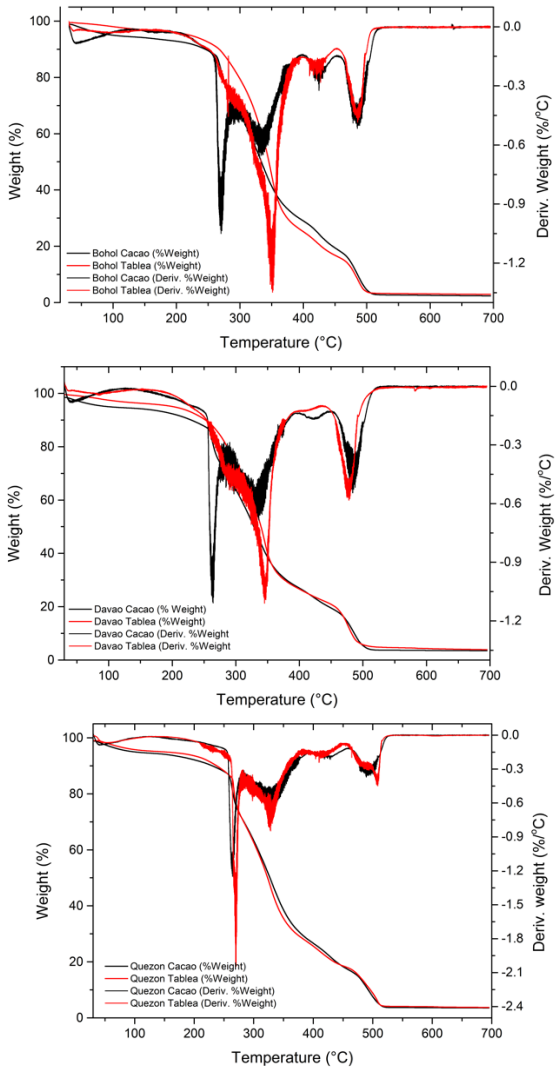

Figure 4: Representative thermogravimetry and DTG curves of (A) Bohol, (B) Davao, and (C) Quezon samples.

The specific weight contributions of the components that underwent thermal degradation as well as their thermal parameters are tabulated in Table 9. Across all samples, moisture content ranged from 2.00 % to 4.35% of its overall weight, which satisfied the water level cut-off at 7.5% as per the Philippine National Standard for Philippine Tablea ("Bureau of Philippine Standards" 2012; Bureau of Agricultural and Standards 2011). The moisture content measured in TGA was greater compared to the results of the proximate composition analysis. Such difference is due to the temperature scan rate in the different protocols used, which likely accompanied the volatilization of components other than water at temperatures 100-120 °C. The pyrolysis of polysaccharides accounted for between 18.78% and 26.15% of weight. The most significant weight contribution was attributed to the release of cacao liquor and thermal degradation of fat which encompassed the third and fourth mass loss steps. Residue was the least abundant in terms of mass ranging from 2.55% to 4.05% across all samples.

For all tablea samples, similar mass loss steps were also observed when compared to their cacao counterparts. The TGA profile of QC and QT were similar, which was parallel with that of different cacao varieties from South America before and after roasting (Ostrowska-Ligęza et al. 2021). On the other hand, different TGA profiles were obtained for the cacao and tablea samples from Bohol and Davao. For Bohol, there were two shifts observed. First is that the TGA profile of BT is smoother from 30 °C to 350 °C compared to BC. Second, there was less weight contribution in the TGA profile of BT from 350 °C to 500 °C than BC. With the Davao samples, only the smoothening of the DT curve from 30 °C to 350 °C was observed. When comparing the thermal degradation of cacao and its tablea counterparts, a characteristic pattern did not emerge. This is due to the complex composition of the samples studied and the variability of the manufacturing methods used in the making of tablea in the different regions of the Philippines.

Table 6. Thermal degradation parameters obtained from the cacao and tablea samples.

	BC	BT	DC	DT	QC	QT
Moisture loss Temperature range=30-120°C						
onset (°C)	38.56±0	61.15±0.33	38.66±0.35	51.86±5.17	38.81±0.45	40.75±1.27
endset (°C)	76.70±1.36	107.60±2.92	75.26±0.92	98.51±1.46	77.54±1.42	84.69±0.88
midpoint (°C)	58.77±0.69	83.82±1.02	58.06±0.35	75.19±2.79	59.01±0.51	63.00±1.02
change normalized (%)	4.35±0.06	2.00±0.01	3.98±0.07	2.65±0.17	4.37±0.03	3.56±0.18
Pyrolysis of polysaccharides Temperature range=120-280°C						
onset (°C)	258.91±0.13	252.93±0.06	252.77±1.56	250.59±1.65	253.74±0.42	259.67±0.15
endset (°C)	270.30±1.52	275.91±0.01	264.54±0.19	276.26±0.06	264.73±0.08	270.91±1.43
midpoint (°C)	263.47±1.22	260.76±0.66	256.21±0.06	257.71±0.82	257.94±0.40	261.64±1.11
change normalized (%)	21.30±3.01	11.16±0.72	24.89±1.56	14.75±0.77	24.86±0.02	24.21±2.59
Decomposition of fat and release of cocoa liquor Temperature range=280-385°C						
onset (°C)	312.87±5.27	332.24±8.25	310.75±0.19	328.9±0.03	307.49±0.95	314.03±3.32
endset (°C)	355.32±1.43	358.44±2.22	355.44±0.18	356.61±0.40	355.24±0.28	349.73±4.44
midpoint (°C)	334.09±3.35	344.94±2.94	333.10±0.01	342.77±0.21	331.37±0.62	331.88±3.72
change normalized (%)	44.48±0.28	60.59±2.43	42.58±0.59	54.29±0.13	42.50±0.13	44.41±1.61
Decomposition of fat and release of cocoa liquor Temperature range=385-455°C						
onset (°C)	445.50±36.97	416.90±0.93	416.04±2.09	388.85±3.16	417.08±10.74	403.07±5.58
endset (°C)	466.09±49.09	436.32±0.41	433.71±1.84	396.25±20.46	439.23±1.97	434.15±1.87
midpoint (°C)	456.30±42.32	426.83±0.26	424.98±1.85	393.01±11.88	428.17±6.36	418.76±3.85
change normalized (%)	13.40±3.81	11.06±0.51	9.62±0.89	7.47±1.40	11.16±0.24	10.12±0.68
Further degradation of organic compounds and proteins Temperature range=455-520°C						
onset (°C)	445.84±40.65	472.90±0.54	472.37±1.09	467.18±0.91	474.1±3.04	479.74±4.34
endset (°C)	469.99±46.37	497.05±0.47	499.13±0.93	488.90±1.26	503.77±5.381	510.36±0.99
midpoint (°C)	457.90±43.53	484.98±0.51	485.75±0.07	478.04±1.00	488.93±4.207	493.57±2.28
change normalized (%)	13.53±1.29	12.68±0.44	15.40±0.40	14.54±0.76	14.74±1.173	13.98±0.37
Residue						
Residue (mg)	0.16±0.03	0.22±0.03	0.22±0.05	0.24±0.01	0.21±0.01	0.53±0.26
Residue Percent (%)	2.55±0.23	3.12±0.26	3.48±0.03	4.05±0.16	3.26±0.41	3.81±0.14

CONCLUSION

The composition and thermal properties of cacao and tablea from Bohol, Davao, and Quezon were characterized in this study. Proximate composition revealed a decrease in moisture from cacao to tablea in all samples due to the roasting process. FTIR analyses showed the probable presence of phenolics, polysaccharides, carboxylic acids, aldehydes, ketones, fatty acids, and proteins in the analyzed cocoa bean and tablea samples. The GC-MS analysis revealed a total of 27 organic compounds in the volatile profile of cacao and tablea. There were notable differences in the fatty acids, primarily palmitic, stearic, and oleic, which contribute to polymorphism. Across all cacao and tablea samples, the native cocoa butter structure was polymorph form V which is the ideal structure for optimal texture, appearance, and flavor release. This study demonstrated the dynamic transformation of cocoa butter into more stable polymorphs, which suggested the progression of fat bloom. TGA was useful in determining the degradation of components such as polysaccharides, cocoa butter, and proteins. However, no discernible shifts are observed in the DSC and TGA thermograms that distinguish the cacao samples and their tablea counterparts. Based on these findings, future research may consider the performance of increased GC-MS trials and Sn-2 positional fatty acid analysis by pancreatic lipase to determine the fatty acid profile of the samples.

Considering the increasing demand for cacao and tablea, the composition and thermal properties assessed from this study may aid manufacturers in product development per the Code of Practice for Philippine Tablea (PNS/BAFS 88:2012). Additionally, the lack of national standard on the use of a single variety of cacao in tablea making is both a challenge and an opportunity in exploring the best variety or mix of varieties that will result in a tablea product with the optimal taste and quality. Additionally, the exploratory results reported and experiments performed in this study may benefit manufacturers in optimizing processes and storage conditions for producing high-quality Philippine tablea and developing techniques that detect adulteration.

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CONFLICT OF INTEREST

The authors declare no conflict of interest.

CONTRIBUTIONS OF INDIVIDUAL AUTHORS

All authors have contributed to the conceptualization, experimentation, data analysis and writing of the paper. Additionally, revisions and editing were made by Adaptar, Bonto, Nuñez, and Tan.

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SUPPLEMENTARY INFORMATION

Table S1. Composition of DSC-soaked extracts of cacao and tablea.

	Compound	Functionality	Sample Code	RT (min)[a]	RI[b]	% Peak Area	Sample code	RT (min)[a]	RI[b]	% Peak Area
1	Ethyl stearate	fatty acid ester		74.34	2092	8.10				
2	Ethyl oleate	fatty acid ester		73.03	2064	5.60				
3	Ethyl-9,12-octadecadienoate	fatty acid ester		72.71	2057	3.90				
4	Ethyl palmitate	fatty acid methyl ester		64.66	1892	65.80				
5	Methyl palmitate	fatty acid methyl ester						60.79	1823	6.60
6	Methyl stearate	fatty acid methyl ester						71.14	2023	5.60
7	Stearic acid	saturated fatty acid						73.92	2083	31.50
8	Palmitic acid	saturated fatty acid	**BC**				**BT**	64.53	1890	22.80
9	γ-Tocopherol	tocopherol		109.19	3034	3.00		109.23	3035	2.10
10	Stigmasterol	phytosterol		114.36	3230	5.70		114.83	3244	1.60
11	γ-Sitosterol	phytosterol		116.34	3289	4.70		116.82	3303	7.00
12	2-Heptadecanone	ketone						55.99	1744	4.60
13	2-Nonadecanone	ketone						70.01	1999	2.40
14	α,α-diphenyl-benzenemethanol	carbinol						71.95	2041	6.80
15	Ethyl iso-allocholate	allocholate derivative		113.28	3198	3.20				
16	Caffeine	purine, methylxanthine alkaloid						55.76	1741	9.20
1	Palmitic acid	saturated fatty acid		65.08	1853	26.5		63.91	1879	18.6
2	Stearic acid	unsaturated fatty acid		74.71	2100	32.0		73.49	2074	10.2
3	trans-δ9-Octadecenoic acid	unsaturated fatty acid		73.62	2077	27.0				
4	Oleic acid	unsaturated fatty acid		70.09	2000	1.9				
5	Methyl palmitate	fatty acid methyl ester						60.79	1823	2.0
6	Ethyl palmitate	fatty acid ester						64.55	1890	10.4
7	Ethyl stearate	fatty acid ester						74.24	2090	5.3
8	Ethyl ester tetradecanoic acid	fatty acid ester						52.59	1693	0.7
9	γ-Tocopherol	tocopherol						109.24	3036	3.6
10	Stigmasterol	phytosterol		114.74	3241	1.6		114.87	3245	3.9
11	β-Sitosterol	phytosterol	**DC**	116.77	3301	1.5	**DT**	116.85	3303	10.1
12	Caffeine	purine, methylxanthine		56.08	1746	4.9		55.77	1741	21.2
13	2-Nonadecanone	ketone						69.98	1998	3.2
14	2-Heptadecanone	ketone						63.91	1879	18.6
15	Triphenylmethane	triarylmethane						64.27	1885	5.9
16	2,2'-Methylene-bis(6-tert-butyl)-para-cresol	cresol derivative		83.86	2318	1.9				
17	Bis(2-ethylhexyl) isophthalate	isophthalate		100.22	2651	2.6				
18	5-Methyl-2-phenyl-2-hexenal	phenylacetaldehydes						29.75	1390	1.0
19	Benzophenone	diarylketone						38.32	1521	0.5
20	hexahydro-3-(2-methylpropyl)-pyrrolo[1,2-	diverse functional groups						54.27	1717	2.2

	a]pyrazine-1,4-dione									
1	Ethyl oleate	fatty acid ester		73.01	2064	7.8				
2	Ethyl-9,12-octadecadienoate	fatty acid ester		72.69	2057	5.3				
3	Ethyl palmitate	fatty acid ester		64.66	1892	3.8		64.57	1891	6.2
4	Ethyl stearate	fatty acid ester		74.34	2092	2.8		78.73	2193	1.1
7	Methyl 10-octadecenoic acid	fatty acid methyl ester						69.74	1993	1.9
8	Methyl palmitate	fatty acid methyl ester						60.81	1823	1.7
9	Methyl stearate	fatty acid methyl ester						71.12	2023	1.7
10	Palmitic acid	saturated fatty acid						64.05	1881	16.6
11	Stearic acid	saturated fatty acid	**QC**				**QT**	74.26	2091	4.2
12	Oleic Acid	unsaturated fatty acid						72.58	2054	45.0
13	γ-Tocopherol	tocopherol		109.21	3035	5.4		109.24	3036	1.3
14	Stigmasterol	phytosterol		114.38	3231	4.5		114.86	3245	2.3
15	β-Sitosterol	phytosterol		116.36	3289	4.6		116.88	3304	4.3
16	Caffeine	purine, methylxanthine alkaloid		56.00	1744	62.8		56.51	1753	0.6
17	2-Heptadecanone	ketone						59.34	1797	0.9
18	2-Nonadecanone	ketone						70.00	1998	1.4
19	Bis(2-ethylhexyl) isophthalate	isophthalate		99.90	2643	3.0				
20	α,α-diphenyl-benzenemethanol	carbinol						71.92	2040	10.7

[(a)]Retention Time and [(b)]Retention index (HP 5ms column)