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Characterization of chemical and volatile compounds in cocoa beans (*Theobroma cacao*) from highland and lowland areas of Bantaeng, South Sulawesi

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Abstract

Characterization of Chemical and Volatile compounds of cocoa from highlands and lowlands have not been reported in scientific journals. Therefore, this study aims to determinethe Characterization of Chemical and Volatile compounds of cocoa beans from highland and lowland regions. Cocoa beans were extracted using Maceration method and analyzed by Gas Chromatography-Mass Spectrometry (GC-MS). The results of this study indicate that the highest free fatty acid content (FFA) of 7.18% was obtained in sample from the highland with 3 days of fermentation, the highest water content (4.29%) was obtained incocoa beans sample from lowland with 5 days of fermentation, the highest ash content (4.28%) was obtained in cocoa beans sample from lowland with 3 days of fermentation, the highest protein content (13.32%) was obtained in sample from the highland with 5 days of fermentation, and the highest fat content (49.85%) was obtained incocoa beans sample from lowland with 3 days offermentation. Another differentiating characteristic between cocoa beans from lowland and highland was the occurrenceofn-Hexadecanoic acid and 3,7-dimethyl-3,7-dihydro-1h-purine-2,6-dione- in samples from lowland.

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Fermentation,
Volatile compounds,
Growing altitude

1. Introduction

Cocoa is one of the leading commodities that can enhance industrial economic growth. At present, the majority of Indonesian cocoa beans produced are bulk cocoa beans, and only a few plantations produce fine cocoa beans.

Cocoa production in South Sulawesi in 2017 reached 134,090 tons with an area of 238,760 hectares of smallholder plantations spread across 22 regencies, mainly Luwu, Bone, Wajo, Soppeng, Pinrang, Bulukumba and Bantaeng Dinas Perkebunan, 2017.

The amount of cocoa produced by Indonesia is not followed by the quality that can compete with the products from other countries, especially about quality standards, pre-harvest, and post-harvest handling. Some of the reasons for the low quality of cocoa beans are due to the little knowledge of farmers in handling foodstuffs.

Although the efforts made cocoa beans to improve good quality, it still difficult to find dry cocoa beans of good quality and uniform, especially cocoa beans produced by smallholder plantations. Because most people's farms do not yet have adequate processing facilities and skilled personnel, so the location is very isolated from the marketing site. Some of the things mentioned above indirectly determine the cocoa beans produced, besides the

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quality of cocoa beans are also influenced by several factors such as soil and environmental conditions, clones, cultivation techniques, post-harvest handling techniques.

Based on the description above, the authors took the initiative to research to determine characterization of chemical and volatile compounds with cocoa beans found in the high and low areas of Bantaeng district. Also, cocoa beans from different plains function as indicators to distinguish good quality cocoa beans. Thus this research can produce information on volatile compounds for further research applications

2. Materials and Methods

The main ingredients used are cocoa beans in the highlands of Tompobulo District and low areas in Gantarangkeke Subdistrict, Bantaeng Regency. The chemicals used are dichloromethane, pentane, sodium sulfate anhydrous, sodium chloride (Merck, Darmstadt, Germany). The alkane standard (C8-C22) and the standard internal 1,4-dichlorobenzene from Sigma Aldrich, Steinhein, Germany, propylene glycol from PT. Brataco Chemika (Indonesia). Supporting materials used are standard scents such as maltol, ethyl methyl-2-butyrate, diethyl disulfide, hexanal, acetyl pyridine, and 2-methyl butanol from PT. Mane Flavor and Fragrance (Indonesia).

The tools used are 250 ml Erlenmeyer tubes, analytical scales, thermometers, pipettes, porcelain cups, ovens, soxhlet flasks, measuring cups, water baths, desiccators, pH gauges, Kjeldahl flasks, hotplates, furnaces, and tools used for analysis volatile compound GC-MS (Gas Chromatography-Mass Spectrometry) GCMS-QP 2010 SHIMADZU.

2.1. Research Method

Dried cocoa beans used in this study are cocoa beans obtained from two different regions, the high area of Tompobulu District and the low area in Gantarangkeke Subdistrict, Bantaeng Regency, those cocoa beans referred as A1 and A2 cocoa beans. The selected cocoa is then the process of making cocoa powder. Making cocoa powder refers to the Jumriah (2011) method, with modifications to the process steps (1). The stages of the dry cocoa bean process are as follows; firstly the 4-5 month-old cacao fruit is picked from the tree, second, it ferments in sacks for 3 and 5 days, third a 4-hour immersion and washes to clean up the remnants of the pulp attached to the skin of the cocoa beans, the fourth was sun drying for 2-3 days, the fifth stripped the shell of the seeds to get the cocoa beans. Furthermore, cocoa beans are blended.

2.2. Physico-Chemical Analysis Procedures and GC-MS Analysis

The dried cocoa beans produced were analyzed by Chemical Physics in the form of analysis of FFA levels, water content, ash content, protein content, fat content and for concentrated dried cocoa beans extracts were analyzed using capillary column chromatography which is connected with a mass spectrometer to identify the composition of volatile components.

2.3. Research Design

The design used in this study is a Completely Randomized Design (CRD) with two factors, namely:

A. Factor A: Location of cocoa

a) A1: Highland location of cocoa (Tompobulo)

b) A2: Lowland location of cocoa (Gantarangkeke)

B. Factor B: Duration of Fermentation
a) B1: Fermentation for 3 days.
b) B2: Fermentation for 5 days.

There are 4 treatments and 3 times repetition of physicochemical test results. To find out the effect of treatment, an Analysis of Variance Procedure (ANOVA) is carried out. If there is a real effect between treatments, an LSD test (the smallest significant difference) with a 95% confidence level is used with the help of the Minitab® program Ver 17.1.0. with a significance of $p<0.05$ between the mean values to see the difference between treatments

3. Results and Discussion

3.1. Free Fatty Acid (FFA)

Based on the results of the study, the average value of dry cocoa beans FFA levels in Bantaeng Regency ranged from 1.93 to 7.18%. The lowest FFA level was in treatment, Gantarangkeke Subdistrict low area location with 5 days fermentation time, while the highest FFA level was in the treatment with high area location in Tompobulo District with 3 days fermentation time. Based on ANOVA results, it showed that the treatment had a significant effect ($p <0.05$) on the FFA results. BNT further test results at a 95% confidence level showed that each treatment was different. The results of the analysis of FFA levels of dry cocoa beans in Bantaeng Regency can be seen in Figure 1.

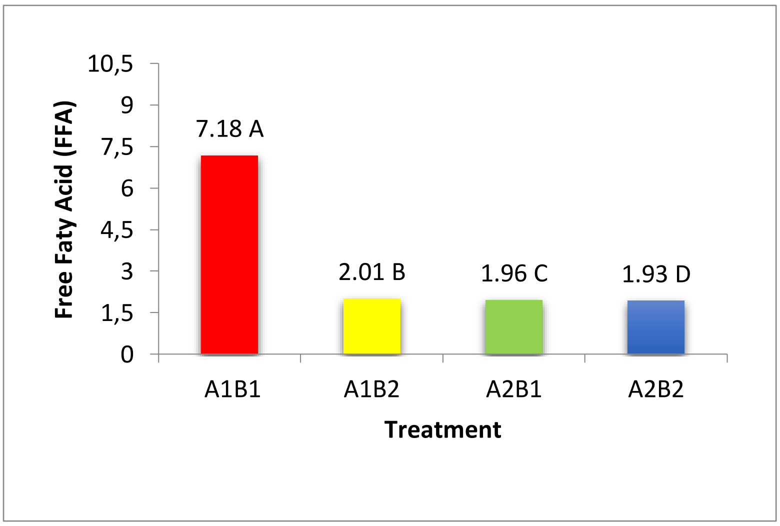

Figure 1. The water content of corn flour.

The results of research by Liyanda et al. (2012) showed that altitude influenced cocoa fat production and fat content (2). The higher the place of planting cocoa, the lower the temperature, so the higher the level of cocoa butter produced.

3.2. Water Content

Water content is very important in determining the durability of food ingredients because it affects physical, chemical, microbiological changes and enzymatic changes.

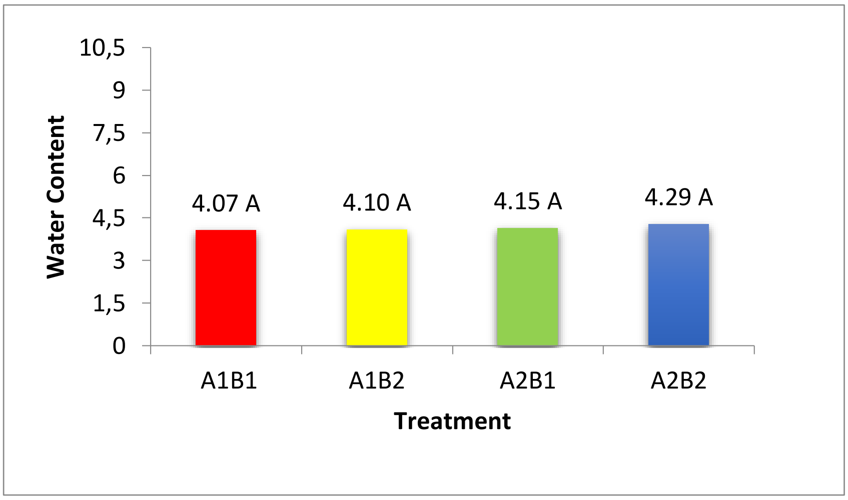

Figure 2. Percentage of dry cocoa beans water content in Bantaeng Regency

The moisture content of the dried cocoa beans was lower than the quality standard of SNI 2323-2008, which maximum is 7.5% but higher than the dried cocoa beans by Jumiati et al (2018), which is equal to (3.53%) (3). The difference in water content obtained is greatly influenced by the method of making dried cocoa beans. The process of increasing water content during storage is a result of the process of adsorption of water vapor. The water adsorption process will occur when the water vapor pressure in the storage air is higher than the water vapor pressure on the surface of the dried beans (4). Plastic sacks made the water levels increased due to the occurrence of the process of entry of water into the package even though it is quite small and increased water content (5).

3.3. Ash Content

Sulfur compounds are also found in cocoa beans. This mineral is needed for healthy skin, hair, and nail growth. Based on the results, the average value of dried cocoa beans ash content in Bantaeng Regency obtained ranged from 3.84-4.28%.

Based on the results, the average value of dried cocoa beans ash content in Bantaeng Regency obtained ranged from 3.84-4.28%. The lowest ash content was obtained in the treatment, namely with a high location of the Tompobulo District with a fermentation period of 3 days, while the highest ash content was obtained in the treatment with a low location of the Gantarangkeke District with 3-day fermentation time. Based on ANOVA results, it showed that the treatment did not have a significant effect ($p > 0.05$) on the ash results. The results of the analysis of ash content of dry cocoa beans in Bantaeng Regency can be seen in Figure 3.

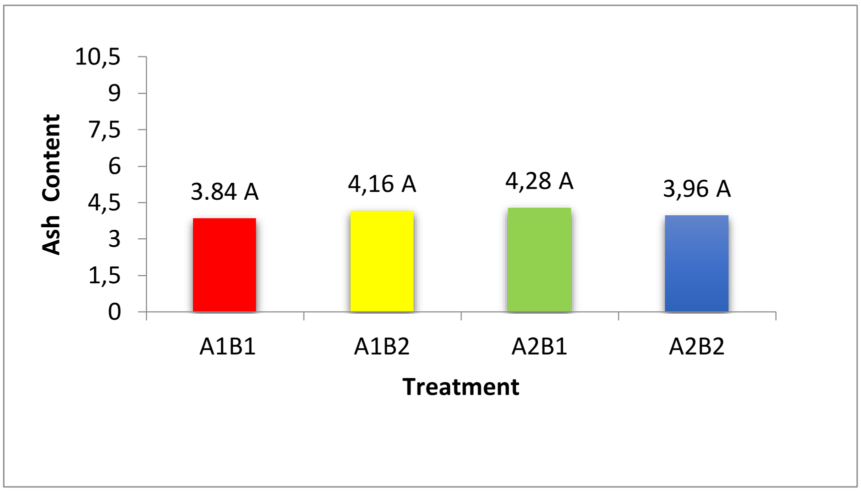

Figure 3. Percentage of dry cocoa beans ash content in Bantaeng Regency

From the results of the study, the ash content in dry cocoa beans decreased due to the previous cacao beans having undergone a drying process which caused some of the ash content to be reduced. In accordance with the opinion of Pratama (2011), that fresh ingredients before undergoing processing have ash content and other mineral content contained in these materials are still intact. Unlike the case with materials that have undergone various processing processes, some of the ash and minerals disappear from the material. Another thing that causes a reduction in ash content is due to high drying temperatures so that the ash content in the material evaporates.

3.4. Protein Content

Based on the study, the average value of the protein content of dried cocoa beans in Bantaeng Regency obtained from 12.01-13.32%. The lowest protein level was in the treatment, great location of Tompobulo District with 3 days fermentation, while the highest protein content was in the treatment in a high location area of Tompobulo District with 5 days of fermentation. Based on ANOVA results showed that the treatment had a significant effect ($p < 0.05$) on protein yields. The analysis results of the dried cocoa beans protein content Bantaeng Regency can be seen in Figure 4.

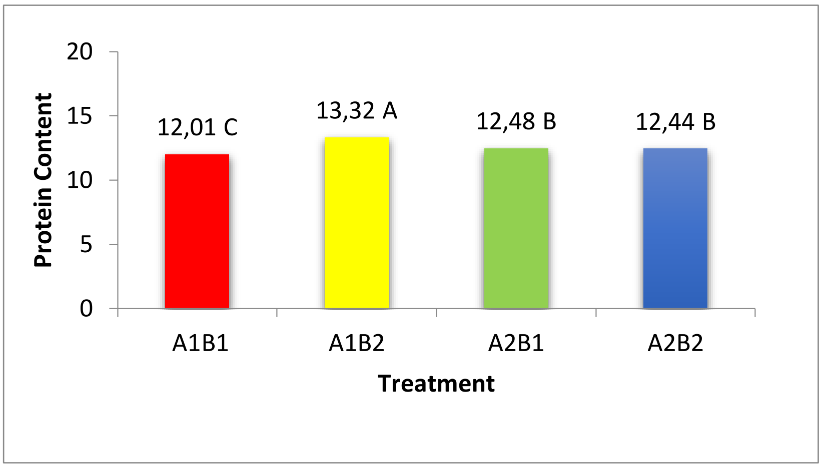

Figure 4. Percentage of dried cocoa beans protein content in Bantaeng District

The high protein content in the treatment was allegedly due to the long storage time in the plastic sack causing heat in the cocoa beans so that there was a reshuffle of components inside the cocoa beans. These components overhaul is one of the causes of increased protein content compared to other treatments, with increased protein content causing a decrease in water content in cocoa beans with the results of research conducted (Jumiati et al. 2018) (3).

3.5. Fat Content

Mulato and Sukrisno (2003b), the fat content range in Indonesian cocoa beans is 49-52%. While the cocoa beans used in this study contain about 45.41% fat content (6). The results of the analysis of the fat content of dried cocoa beans Bantaeng can be seen in Figure 5.

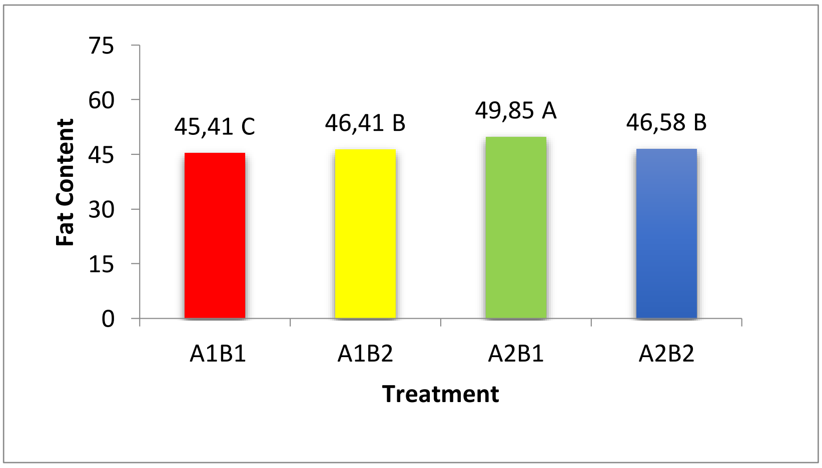

Figure 5. The results of the analysis of the fat content of dried cocoa beans of Bantaeng

Based on the study results, the average value of fat content of dry cocoa beans in Bantaeng Regency was obtained in the range of 45.41-49.85%. The lowest fat content was in the treatment, namely the location of the high area of Tompobulo District with 3 days fermentation time. The highest fat content was obtained in treatment in the low location area of Gantarangkeke District with 3 days fermentation time. Based on ANOVA results showed that the treatment had a significant effect ($p < 0.05$) on fat yield. BNT further test results at 95% confidence level showed that A1B1 treatment was different from A1B2, A2B1, and A2B2 treatments. The A1B2 treatment was different from the A2B1 treatment, but it was not different from the A2B2 treatment, the A2B1 treatment was different from the A2B2 treatment. The type of plant material determines fat content and seasonal factors.

3.6. Volatile Component

Volatile compounds cause aromas in chocolate due to the Maillard reaction and the degradation of Stecker (7). Components of chocolate flavor about 600 volatile compounds with a very complicated arrangement (8). The volatile components are aldehydes, ketones, esters, alcohols, acids, pyrazines, quinoxalines, furans, pyrones, lactones, pyrrole, and dicopirazines. Different types of cocoa can produce different flavor components (9).

3.7. Dried Cocoa Beans in Tompobulu District

Based on the identification using GC-MS with the DB-Wax column, 5 volatile components were detected in the dry cocoa beans in the Tompobulo sub-district for 3 days. Raw cocoa beans contain about 4% methylxanthines (10). Theobromine (3,7-dimethylxanthine) is the principal alkaloid of cocoa (2% to 3%). Caffeine (1,3,7-trimethylxanthine) only found in small amounts (0.2%), and theophylline. All contribute to the bitter taste typical of cocoa (11). Total Ion Chromatogram (TIC) 3 days dry fermented cocoa beans in Tompobulo District Figure 6.

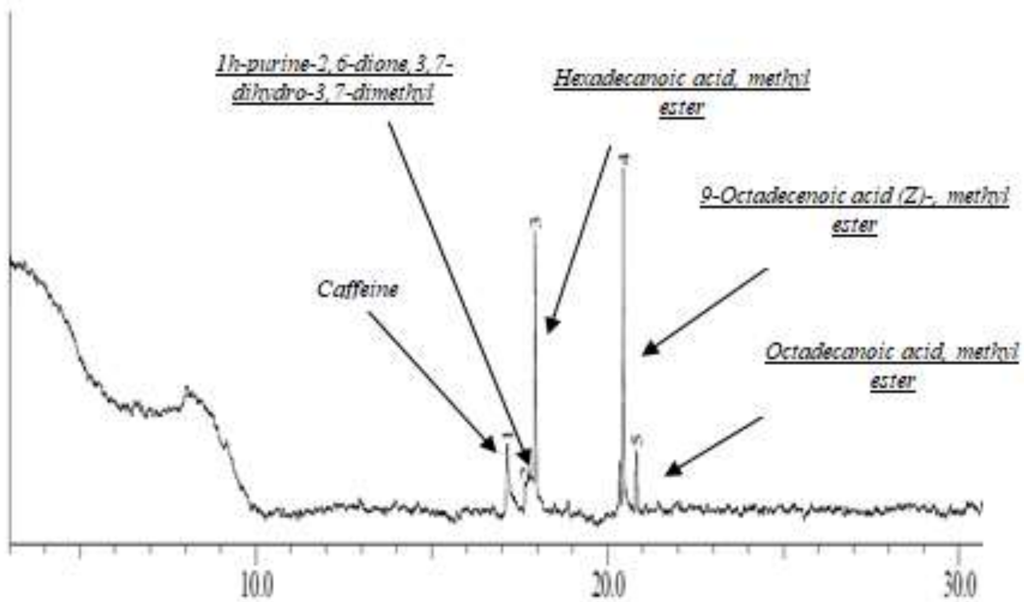

Figure 6. Total Ion Chromatogram (TIC) Dry cocoa beans in Tompobulo District for 3 days fermentation

In the dried cocoa bean in Tompobulo District fermentation for 3 days detected the component of Caffeine (1,3,7-trimethylxanthine), 1h-purine-2,6-dione, 3,7-dihydro-3,7-dimethyl, Hexadecanoic acid, methyl ester, 9-Octadecenoic acid (Z) -, methyl ester and Octadecanoic acid, methyl ester. The largest area of the 9-Octadecenoic acid (Z) - volatile compound, methyl ester, was found in the dry cocoa beans in Tompobulu sub-district for 3 days at 37.57%.

Based on the identification used GC-MS with the DB-Wax column, 5 volatile components were detected in the dry cocoa beans in Tompobulo sub-district for 5 days. 1h-purine-2,6-dione, 3,7-dihydro-3,7-dimethyl, Hexadecanoic acid, methyl ester, 9-Octadecenoic acid (Z) -, methyl ester and Octadecanoic acid, methyl ester. The largest area of volatile compounds 1h-purine-2,6-dione 3,7-dihydro-3,7-dimethyl was found in dry cocoa beans in Tompobulu sub-district for 5 days, that was 34.96%. Total Ion Chromatogram (TIC) Dry cocoa beans in Tompobulo District for 5 days fermentation can be seen in Figure 7.

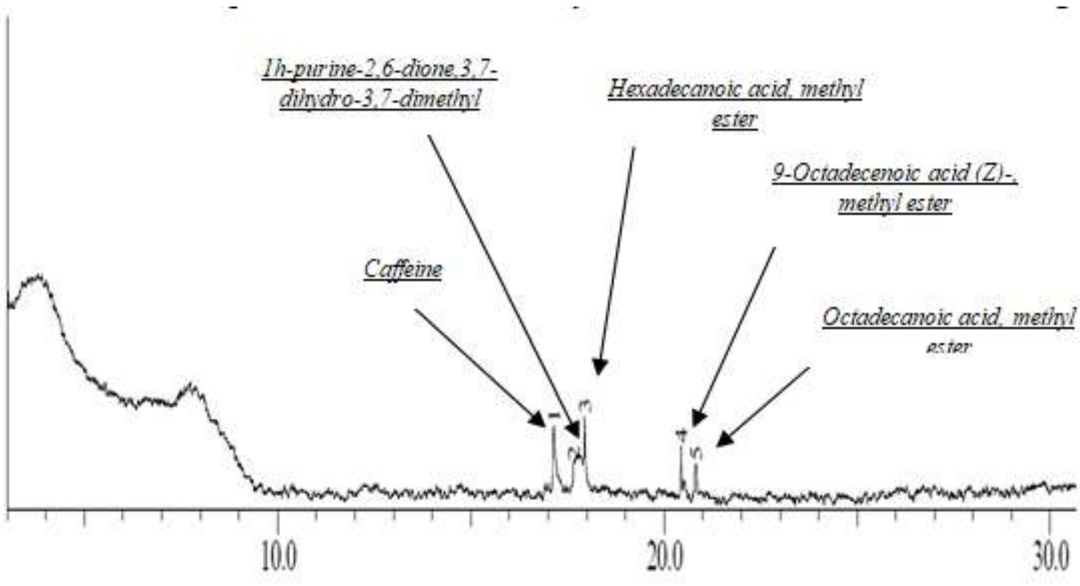

Figure 7. Total Ion Chromatogram (TIC) Dry cocoa beans in Tompobulo District for 5 days fermentation.

3.8. Dried Cocoa Beans in Gantarangkeke District

Based on the identification used the GC-MS with the DB-Wax column, 5 volatile components were detected in the dried cocoa beans in Gantarangkeke sub-district for 3 days fermentation. The dried cocoa beans in Gantarangkeke District, fermentation for 3 days was detected by the component Caffeine (1,3,7-trimethylxanthine), 3,7-dimethyl-3,7-dihydro-1h-purine-2,6-dione, Hexadecanoic acid, methyl ester, 9-Octadecenoic acid (Z) -, methyl ester and Octadecanoic acid, methyl ester.

The largest area of 3,7-dimethyl-3,7-dihydro-1h-purine-2,6-dione volatile compound was found in the dried cocoa beans of Gantarangkeke District for 3 days fermentation at 50.55%. Total Ion Chromatogram (TIC) Dry cocoa beans in Gantarangkeke District for 3 days fermentation can be seen in Figure 8.

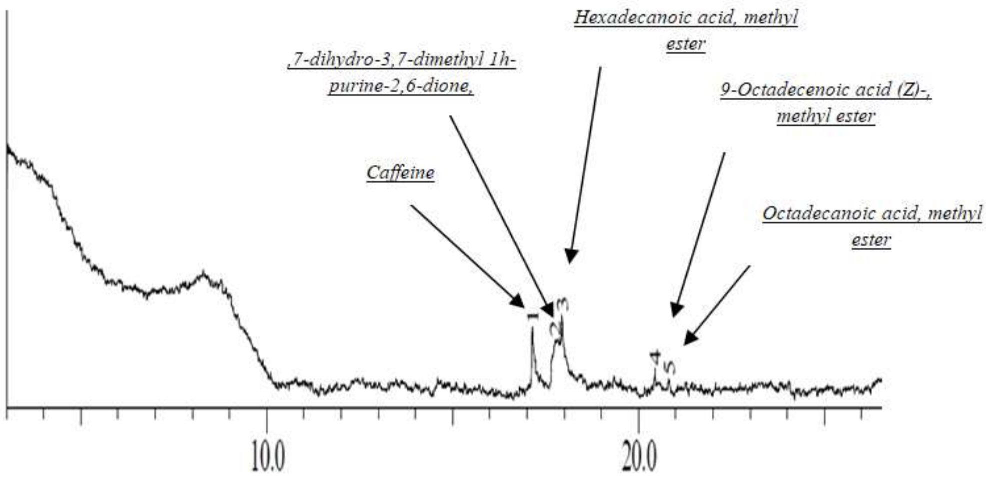

Figure 8. Total Ion Chromatogram (TIC) Dry cocoa beans in Gantarangkeke District for 3 days fermentation.

Based on the identification using GC-MS with the DB-Wax column, 5 volatile components were detected in the dry cocoa beans in Gantarangkeke sub-district for 5 days. In dry cocoa beans in Gantarangkeke District for 5 days fermentation, the detection of Caffeine components (1,3,7-trimethylxanthine), Hexadecanoic acid, methyl ester, n-Hexadecanoic, 9-Octadecenoic acid (Z) -, methyl ester and Octadecanoic acid, methyl ester.

The largest area of Caffeine volatile compounds is found in the dry cocoa beans in Gantarangkeke District for 5 days fermentation at 30.62%. Total Ion Chromatogram (TIC) Dry cocoa beans in Gantarangkeke District for 3 days fermentation can be seen in Figure 9.

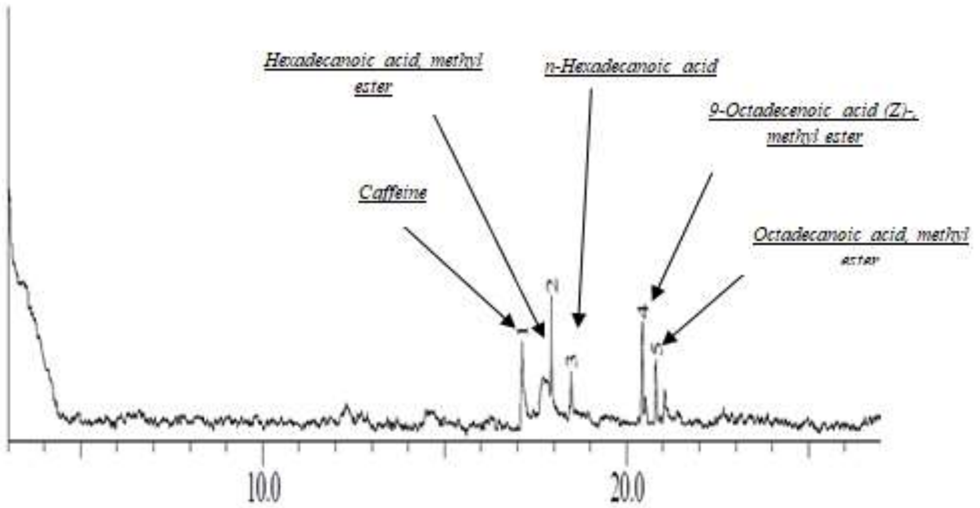

Figure 9. Total Ion Chromatogram (TIC) Dry cocoa beans in Gantarangkeke District for 3 days fermentation.

4. Conclusions

Based on this study it can be concluded that: free fat content (FFA) water content, ash content, protein content and highest fat content of the highest free fat content (FFA) was the cocoa beans in the high region with 3 days fermentation time (A1B1) namely (7, 18%), the highest yield of water content was in the low area cocoa beans with 5 days fermentation time (A1B2) 4.29%, the highest ash content result was in the low area cocoa beans with 3 days fermentation time (A2B1) 4.28%, The highest protein content result was in the high area cocoa beans with 5 days fermentation time (A1B2) 13.32%, the highest fat content results in the location of low area cocoa beans with 3 days fermentation time (A2B1) 49.85%. Volatile compounds detected in dry cocoa beans Tompobulo District were 5 volatile components. In dried cocoa beans Gantarangkeke was detected 6 volatile components.

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