J Food Sci Technol (September 2019) 56(9):4323–4332
https://doi.org/10.1007/s13197-019-03901-8

ORIGINAL ARTICLE

Sensory and physicochemical characteristics of dark chocolate bar with addition of cinnamon (*Cinnamomum burmannii*) bark oleoresin microcapsule

Danar Praseptiangga[1] · **Syuga Eugenia Invicta**[1] · **Lia Umi Khasanah**[1]

Revised: 20 March 2019 / Accepted: 24 June 2019 / Published online: 8 July 2019

Abstract Indonesia is one of the world's most prominent producers of cocoa and cinnamon. Dark chocolate bars and *Cinnamomum burmannii* are rich in antioxidants. The addition of a cinnamon oleoresin to a dark chocolate bar has not been previously studied due to its strong consistency and sticky texture. Microencapsulation was used to cover the undesirable properties of oleoresin, and the addition of cinnamon bark oleoresin microcapsules was expected to improve the functional properties and influence the characteristics of dark chocolate bars. This study aimed to determine the effects of adding various concentrations of cinnamon bark oleoresin microcapsules (4%/F1, 6%/F2, and 8%/F3) to dark chocolates bars on their sensory, physical, and chemical characteristics and to define the best formula of a dark chocolate bar. The results showed that various concentrations of cinnamon bark oleoresin microcapsules led different trends for each evaluation, and the best formula resulted from the addition of cinnamon bark oleoresin microcapsules to a dark chocolate bar (8%) that is accepted by the panellists. This bar had the hardest texture, the highest total phenol and antioxidant activities, and the lowest moisture content, and it was classified as having a high potency of vitamin E (tocopherol).

Keywords Dark chocolate bar · Cinnamon bark oleoresin microcapsule · Sensory characteristics · Physicochemical characteristics

✉ Danar Praseptiangga
dpraseptiangga@staff.uns.ac.id

[1] Department of Food Science and Technology, Faculty of Agriculture, Universitas Sebelas Maret (UNS), Jl. Ir Sutami 36 A Kentingan, Surakarta, Central Java 57126, Indonesia

Introduction

Indonesia is the third largest cocoa producer in the world after the Ivory Coast and Ghana (Dwijatmoko et al. 2016). In 2016, cocoa bean production in Indonesia yielded 656,817 tons. The export volume of dry beans and semi-finished products high (> 50%) (Direktorat Jenderal Perkebunan Indonesia 2016) but was relatively low for the chocolate products (finished products). Chocolate industries are mostly found in developing countries that do not have cacao trees (International Cocoa Organization 2017).

The production of chocolate products, including dark chocolate bars, grows rapidly with the presence of a stable market throughout the world (Dwijatmoko et al. 2016). The world's fondness for dark chocolate bars is caused by their taste and functional effects. A dark chocolate bar is mainly made from cocoa nibs, cocoa butter, cocoa liquor/cocoa mass, sugar, and/or lecithin, which is used as an emulsifier. The total phenolic and flavonoid contents in dark chocolate are two to three times higher than in milk chocolate and white chocolate. The content of theobromine in a commercial dark chocolate bar is 883.11 ± 3.54 mg/100 g, while in milk chocolate, it is 125.154 ± 0.98 g/100 g (Beckett 2008).

Enhancement of the flavour and functionality of chocolate bars involves adding other ingredients. Cinnamon is a widely used spice that is often added to chocolate bars (Dwijatmoko et al. 2016). Exporting 48,900 tons of cinnamon has made Indonesia the largest cinnamon exporter in the world (FAOSTAT 2016). *Cinnamomum burmannii*, which is known as Indonesian cinnamon, is classified as a notable species in the global market (Khasanah et al. 2014).

Based on characterisation by the flow injection mass spectrometric (FIMS) fingerprinting method, *C. burmannii*

has been shown to contain more type-A proanthocyanidins than *Cinnamomum verum*, *Cinnamomum cassia*, and *Cinnamomum loureiroi* (Chen et al. 2014). *Cinnamomum burmannii* contains functional compounds used to overcome digestive problems, diabetes, inflammation, and microbial activity (Muhammad and Dewettinck 2017). Gas chromatography–mass spectrometry showed that cinnamaldehyde is the main component of cinnamon bark oleoresin (Khasanah et al. 2017). Cinnamaldehyde performs anti-inflammatory activity by decreasing nitric oxide (NO) production in lipopolysaccharide-stimulated macrophages. Cinnamaldehyde also activates the peroxisome proliferator-activated receptor to weaken NF-κB, which leads to cancer (Muhammad and Dewettinck 2017). Ethanol extraction of cinnamon bark oleoresin has the antioxidant activity with an IC_{50} value of 8.36 μg/ml (Ervina et al. 2016).

The addition of cinnamon oil and powder to dark chocolate and milk chocolate bars has been observed (Albak and Tekin 2015; Dwijatmoko et al. 2016; Ilmi et al. 2016; Praseptiangga et al. 2018), while the addition of a cinnamon oleoresin has not been previously performed. Oleoresin has a strong consistency and sticky texture. Oleoresin contains volatile bioactive components that may vanish during storage and processing (Irfiana et al. 2017). Cinnamon also has a spicy aroma and taste (Ilmi et al. 2016) that can affect panellist perception. A lower concentration of added cinnamon oleoresin will give a lighter taste but will also give less functional effects.

The undesirable properties of cinnamon oleoresin can be masked by microencapsulation. Microencapsulation protects the active compound in oleoresin by entrapping the compound in shell materials and transforming it into a free-flowing powder that is easier to handle (Irfiana et al. 2017; Muhammad and Dewettinck 2017). The release of the active compound can be controlled by controlling the microcapsule dissolution. One of the factors that influences the dissolution of microcapsules is the solubility of the shell materials (Khasanah et al. 2015).

The shell materials that are usually used include a mixture of arabic gum and maltodextrin. Arabic gum has a good flavour, good oil stabilisation ability and high solubility. Arabic gum needs to be combined with maltodextrin, which is less hygroscopic, to prevent rapid dilution when in contact with saliva. Thus, the release process can be controlled more slowly, and cinnamon's strong flavour can be momentarily covered (Kania et al. 2015).

Microencapsulation of cinnamon bark oleoresin with arabic gum and maltodextrin (3:1) performed by Murti (2012) showed that the water solubility was 94.652% and the aldehyde content was 60.50%; it also had a good uniform wall, and texture ballooning did not occur. To the best of our knowledge, there is no study on the addition of cinnamon bark oleoresin microcapsules to dark chocolate bars. Cinnamon is expected to increase the concentration of functional compounds, especially antioxidants, and also give the signature flavour of Indonesian spices to the dark chocolate bar. Therefore, the effects of cinnamon bark oleoresin microcapsule addition on the properties of dark chocolate bars were evaluated.

Materials and methods

Materials

The primary material used into make dark chocolates bar was TULIP Easy Melts Dark Chocolate Couverture (65% cocoa). The cinnamon bark used for oleoresin microencapsulation was from Girimarto, Wonogiri, Indonesia. Other materials used included 96% ethanol, maltodextrin DE 10, and arabic gum from Agung Jaya, Surakarta, Central Java, Indonesia.

Preparation of cinnamon bark oleoresin microcapsules

Preparation of the one-stage cinnamon bark oleoresin was conducted according to previous studies (Irfiana et al. 2017; Murti 2012) with slight modifications. Dried cinnamon bark with an 11–15% moisture content was milled. Cinnamon powder with a size of 30–50 mesh was then extracted using 96% ethanol (1:6) for 4 h at 70–75 °C. The extraction filtrate was evaporated using a rotary vacuum evaporator at a temperature of 80 °C. The essential oil was prepared according to Irfiana et al. (2017) with modifications. The oil was obtained from 8 h of steam distillation. One-stage oleoresin and essential oil were then blended, and calculations were performed to meet the essential oil content standard based on Khasanah et al. (2017).

Oleoresin microcapsules were prepared according to Irfiana et al. (2017) and Murti (2012) with several modifications. An emulsion was made by homogenizing oleoresin. For the shell materials, Aqua Dest (1:10:40) was used and mixed at a speed of 7600 rpm. The shell materials were a mixture of arabic gum and maltodextrin with a composition of 3:1. The emulsion particle size was then observed with a light microscope. If the particle was uniform and already achieved a micro-size, the homogenisation process was stopped (± 15 min). The emulsion solvent was vaporised using a spray dryer with a feed rate of 15–20 ml/min, an inlet temperature of 100.2 °C, and an exhaust temperature of 74 °C. The size of the microcapsule obtained was then observed.

Preparation of dark chocolate bars

Dark chocolate bars with the addition of cinnamon bark oleoresin microcapsules were prepared based on previous studies (Praseptiangga et al. 2018; Rasuluntari et al. 2016) with several modifications. Cinnamon bark oleoresin microcapsules were added to the melted dark chocolate couverture at the following amounts: 0% (Control/C), 4% (Formula 1/F1), 6% (Formula 2/F2), and 8% (Formula 3/F3). The dark chocolate couverture was used, and cinnamon oleoresin microcapsules were added during the refining-conching process in a ball mill. The ball mill was set to a speed of 90 rpm and stopped if the chocolate particles were micro-sized and uniform (observed every 15 min). Ball milling resulted in a homogenous mixture with particle sizes of 1.71–9.36 μm. The mixture was then hand-tempered using scrapers and knives on a marble table.

Sensory characterisation

The chocolates samples F1, F2, and F3 were evaluated using the hedonic method according to previous studies (Dwijatmoko et al. 2016; Praseptiangga et al. 2018). The sensory attributes were presented on 5-hedonic scales, which were: (1) dislike, (2) rather dislike, (3) neither like nor dislike, (4) rather like, and (5) like.

Physicochemical characterisation

Colour attributes

The colour attributes of the dark chocolate bars with the addition of cinnamon bark oleoresin microcapsules were evaluated using a chroma meter Konika Minolta CR-400 with the CIE L*a*b* method based on previous studies (Dwijatmoko et al. 2016). The L*, a*, and b* values were then used to calculate the hue angle and the total colour difference (TCD). The texture was evaluated using a universal testing machine (UTM) based on Beckett (2008). The room used to evaluate these attributes was set to a temperature of 26–28 °C.

Moisture content

The moisture content was evaluated using the Karl Fischer method and a Moisture Meter CA-200 Mitsubishi Chemical Analytech. The results are presented as the percentage (%) of water in the sample (w/w).

Total phenol and antioxidant activity

The total phenol, antioxidant activity, and 2,2-Diphenyl-1-picrylhydrazyl (DPPH) IC50 evaluations began with maceration extraction of dark chocolate bars. Two types of solvents were used: methanol and acetone:aquades:acetic acid. For the methanolic extract, extraction was performed according to Muhammad et al. (2017) with modifications. One gram of a shredded chocolate bar was dissolved in 20 ml methanol at 80%. The extract was stirred while it was heated at 48–50 °C for 1 h and then filtered. For the acetone:aquades:acetic acid extract, extraction was performed based on Muhammad et al. (2017).

Total phenol evaluation was performed using the Folin Ciocalteu method according to a previous study (Muhammad et al. 2017). Modifications to this study were made and included the addition of 2% Na_2CO_3 that was incubated for 10 min and 0.5 ml Folin–Ciocalteau reagent (1:1) incubated for 30 min. The absorbance was measured with a UV–Vis spectrophotometer at $\lambda = 750$ nm. The antioxidant activity was determined by the IC50 method based on a previous study (Muhammad et al. 2017) with modifications. The chocolate extract concentration was 10^3 ppm, while the DPPH concentration was 10^2 ppm.

GC–MS

Chocolate extraction for GC–MS also used two solvents. The extraction method for the methanolic extract was according to Brunetto et al. (2009) with modifications. One block of the chocolate bar was shredded, added to 13 ml methanol, heated at 110 °C for 2 min, and vortexed for 5 min. The mixture was centrifuged at 5000 rpm for 5 min. For the acetone:aquades:acetic acid extract, extraction was performed based on Muhammad et al. (2017) with slight modifications.

The GC–MS injection method was based on the work of Proestos and Komaitis (2013) with modifications. The methanolic extract (1 μl) was injected with a split ratio of 1/10. The inlet temperature was 290 °C, the MS quad temperature was 150 °C, and the MS source temperature was 230 °C. The oven temperature was kept at 50 °C for 5 min, increased 10 °C/min until 280 °C, and held for 5 min. The acetone:aquades:acetic acid extract (1 μl) was injected at a split ratio of 5:1 and inlet temperature of 250 °C. The oven temperature was kept at 50 °C for 5 min, increased by 10 °C/min until 315 °C, and held for 20 min.

Data analysis

Data were analysed using one-way ANOVA with a significance level of $\alpha = 5\%$. If there was a significant difference in the results, the analysis continued using the Duncan multiple range test.

Results and discussion

Oleoresin is a mixture of a resin, which is used as a taste carrier, and a volatile essential oil, which is used as an aroma carrier (Khasanah et al. 2017). At one stage in this research, oleoresin was blended with an additional essential oil to increase the essential oil content to an amount deemed suitable by the Food and Drug Administration (FDA) and Essential Oil Association of America (EOA) standards. According to the Food and Drug Administration (FDA), the minimum EO content is 25% (Khasanah et al. 2014), while the standard is 18–35% for the Essential Oil Association of America (EOA) (FAO-AGST 2002). One stage oleoresin is made from the extraction of fresh materials with a single-use solvent (Khasanah et al. 2017). The advantages of a one-step oleoresin are time and cost efficiency. The characteristics of the cinnamon oleoresin used in this research are shown in Table 1. Cinnamon oleoresin was then microencapsulated and added to dark chocolate bars to be evaluated.

Sensory properties

According to Table 2, different concentrations of cinnamon bark oleoresin addition did not lead to a significant difference in panellist preference for all sensory attributes. The scoring scale for F1, F2, and F3 was 'rather like', so all the formulas were accepted by the panellists. In previous studies (Dwijatmoko et al. 2016; Ilmi et al. 2016; Praseptiangga et al. 2018; Rasuluntari et al. 2016), the higher the amounts of cinnamon essential oil and powder added, the lower the panellist acceptance of the dark chocolate and milk chocolate bars. This result indicated that the strong flavour of cinnamon could be masked by microencapsulation and that the negative perception of the panellists could be minimised. The largest amount of cinnamon bark oleoresin microcapsules (8%) added to dark chocolates bar did not cause panellist rejection and insignificantly preferred overall.

Table 1 Cinnamon bark oleoresin characteristics

Attributes	Result
One stage oleoresin	
Moisture content of dry cinnamon	12.596%
Yield	10.939%
Essential oil content	19.333%
Color	Reddish brown
Blended oleoresin	
Moisture content of dry cinnamon	13.891%
Essential oil content	21.333%

Colour measurement

The L* value is defined as lightness, which ranges from black (0) to white (100) (Renard and Maingonnat 2012). Samples with cinnamon bark oleoresin microcapsules added had a significantly different lightness than the control. Thus, cinnamon bark oleoresin microcapsule addition increased the lightness of a dark chocolate bar. The value of a* describes the chromatic colour of red (a* positive, + 60) to green (a* negative, − 60), while b* describes the chromatic colour of yellow (b* positive, + 60) to blue (b* negative, − 60) (Renard and Maingonnat 2012). All samples had a positive a* and a positive b*, so the colour of dark chocolate bars with and without the addition of cinnamon bark oleoresin microcapsules are in the chromatic range of red and yellow.

As shown in Table 3, the hue angle of the dark chocolate bars ranged from 18 to 54, which shows that the product colour tends to be red (Ilmi et al. 2016). The hue angle tended to increase with the increase in the cinnamon bark oleoresin microcapsule concentration. The colour of dark chocolate bars with the addition of cinnamon bark oleoresin microcapsules became redder because cinnamon oleoresin is originally a reddish colour (Djafar and Redha 2012). Oleoresin was encapsulated with arabic gum and maltodextrin, which are coloured white, so the oleoresin microcapsule powder had a lighter colour.

The highest concentration (8%) was added to the dark chocolate bar F3, so F3 supposedly has a lighter red colour compared to F2. Differences happen because of several factors, which include homogenization, tempering, or Schiff base formation. Under-tempered chocolate will also result in a lighter colour (Afoakwa 2010).

When the active compound is excessive, cinnamaldehyde will react with an amino acid and induce the formation of a Schiff base. The Schiff base will decrease the intermolecular bond in the polymer chain, so the matrix and pore will be more open (López-Mata et al. 2015). Oleoresin, which has a reddish-brown colour, will escape from the microcapsule and give it a darker colour. Even so, the colour tendency showed no difference.

The TCD calculation was performed to determine the colour difference between the treatment samples and control samples and to determine whether the difference was visible or not. The TCD value, based on Renard and Maingonnat (2012), was either < 0.5 (invisible), 0.5–1.5 (slightly noticeable), 1.5–3.0 (noticeable), 3.0–6.0 (well visible), or > 6.0 (great difference). Meanwhile according to Gao et al. (2008), the threshold necessary for a colour to be recognisably different by the naked eye is > 1.5. As shown in Table 3, the addition of cinnamon bark oleoresin microcapsules had a noticeable effect on the colour difference of the samples. Since the TCD values of F1, F2,

Table 2 Sensory characteristics of dark chocolate bar with addition of cinnamon bark oleoresin microcapsule

Sample	Colour	Appearance (glossiness)	Aroma	Taste	Hardness	Melting capability	Overall
F1	$4.37^{a} \pm 0.76$	$4.37^{a} \pm 0.62$	$4.23^{a} \pm 0.87$	$4.37^{a} \pm 0.81$	$4.27^{a} \pm 0.87$	$4.27^{a} \pm 0.78$	$4.40^{a} \pm 0.67$
F2	$4.33^{a} \pm 0.80$	$4.30^{a} \pm 0.84$	$4.17^{a} \pm 0.95$	$4.40^{a} \pm 0.77$	$4.10^{a} \pm 0.76$	$4.03^{a} \pm 0.96$	$4.27^{a} \pm 0.83$
F3	$4.33^{a} \pm 0.81$	$4.23^{a} \pm 0.86$	$4.33^{a} \pm 0.84$	$4.23^{a} \pm 0.77$	$4.33^{a} \pm 0.61$	$4.13^{a} \pm 0.83$	$4.47^{a} \pm 0.94$

Cinnamon bark oleoresin microcapsule addition F1 = 4%, F2 = 6%, F3 = 8%

Scale 1 = dislike, 2 = rather dislike, 3 = neither like or dislike, 4 = rather like, 5 = like

Within column, mean values marked by different superscript small letters are differ significantly ($\alpha = 0.05$)

Table 3 Texture and colour measurement of dark chocolate bar with addition of cinnamon bark oleoresin microcapsule

Sample	L*	a*	b*	°Hue	TCD	Effect	Hardness (N)
C	$25.44^{a} \pm 0.15$	$8.02^{a} \pm 0.08$	$4.38^{a} \pm 0.08$	$28.61^{a} \pm 0.34$			23.43 ± 1.21^{a}
F1	$27.22^{b} \pm 0.12$	$8.49^{bc} \pm 0.28$	$4.83^{ab} \pm 0.41$	$29.60^{a} \pm 1.38$	1.90	Noticeable	32.96 ± 4.13^{b}
F2	$27.40^{b} \pm 0.30$	$8.63^{c} \pm 0.20$	$5.32^{b} \pm 0.26$	$31.66^{b} \pm 0.71$	2.26	Noticeable	32.97 ± 3.38^{b}
F3	$27.28^{b} \pm 0.15$	$8.32^{b} \pm 0.28$	$4.74^{ab} \pm 0.23$	$29.66^{a} \pm 0.48$	1.90	Noticeable	35.47 ± 3.39^{b}

Cinnamon bark oleoresin microcapsule addition C = 0%, F1 = 4%, F2 = 6%, F3 = 8%

Within column, mean values marked by different superscript small letters are differ significantly ($\alpha = 0.05$)

and F3 were close to the threshold (1.5), a small difference was noticeable; thus, during the sensory evaluation, the panellists did not find the colour to be significantly different.

Texture measurement

According to Table 3, there was a significant difference induced by the addition of cinnamon bark oleoresin microcapsules regarding the hardness of dark chocolate bars. The hardness of the dark chocolate bars increased as the amount of added cinnamon bark oleoresin microcapsule increased, even though there was no significant difference between the treatment samples. The texture of the dark chocolate bar was influenced by refining, conching, and tempering. Tempering is a sequence of processes consisting of cooling, heating, and chocolate inverting to form a chocolate fat crystal β_2 (V form) that is resistant to temperature changes (Afoakwa 2010). Under-tempering causes an increase in chocolate softness, while over-tempering causes an increase in hardness (Ilmi et al. 2016).

The large particle size of chocolate (greater than 30 μm) creates a sandy and rough texture (Beckett 2008). In this study, the particle size of the materials was controlled in the micro-size. A particle size observation was conducted on the emulsion, microcapsule powder, and melting chocolate during ball milling and tempering. The sizes of the emulsion, microcapsule powder, and chocolate fat particle after tempering were 1.58–3.30 μm, 1.18–3.02 μm, and 1.74–7.26 μm, respectively.

A high compactness will increase a product's hardness (Midaryanto and Yuwono 2014). An increase in the product mass with the same volume will increase the compactness. Increasing the cinnamon bark oleoresin microcapsule concentration, which was added to the chocolate mould in the same volume, resulted in an increase in the hardness of chocolate because the microcapsule evenly filled the spaces and cavities in the chocolate.

Moisture content

The moisture content of chocolate is affected by a sequence of processes that uses a thermal treatment, so moisture is primarily decreased in the conching process (Goncalves and Lannes 2010). Referring to Table 4, there was no significant difference in the moisture content from adding cinnamon bark oleoresin microcapsules to dark chocolate bars because of the synced controlling and storing used for all samples.

The percentage of the moisture content insignificantly decreased with the increasing of the cinnamon bark oleoresin microcapsule content added to dark chocolate bars. An increase in the cinnamon bark oleoresin microcapsule concentration will increase the total shell materials in the product, so the total solid content also increases (Kania et al. 2015). The dark chocolate bar moisture content is the result of calculating the percentage of moisture in the sample (w/w). An increase in total solids will increase the weight of the sample. The moisture weight, which is

Table 4 Moisture content, total phenol content, and antioxidant activity of dark chocolate bar with addition of cinnamon bark oleoresin microcapsule

Sample	Moisture content (%)	Total phenol (%)		IC50 (ppm)	
		Met	AAA	Met	AAA
C	$1.78^{a} \pm 0.76$	$5.14^{a} \pm 0.07$	$68.88^{a} \pm 4.12$	$13{,}368.57^{b}$	1573.36^{b}
F1	$1.68^{a} \pm 0.11$	$5.67^{b} \pm 0.07$	$233.14^{b} \pm 2.82$	7250.00^{a}	243.18^{a}
F2	$1.62^{a} \pm 0.24$	$5.73^{b} \pm 0.05$	$257.42^{c} \pm 1.07$	7112.51^{a}	242.67^{a}
F3	$1.55^{a} \pm 0.09$	$6.62^{c} \pm 0.11$	$265.45^{d} \pm 1.94$	5675.68^{a}	209.15^{a}

Met, methanol; AAA, acetone:aquades:acetic acid

Cinnamon bark oleoresin microcapsule addition C = 0%, F1 = 4%, F2 = 6%, F3 = 8%

Within column, mean values marked by different superscript small letters are differ significantly ($\alpha = 0.05$)

relatively the same for higher sample weights, will result in a lower moisture content.

In this research, arabic gum and maltodextrin were used as shell materials. Maltodextrin has a low molecular weight and a simple structure, so water evaporates more easily during the drying process. Moreover, maltodextrin with DE-10 is less hygroscopic and has a rapid drying rate, so it is not easy to reabsorb water (Kania et al. 2015). Beckett (2008) stated that the maximum moisture content in chocolate should be 2% to prevent the growth of microbes. A high moisture content can cause blooming (Afoakwa 2010) and a soft texture (Goncalves and Lannes 2010).

Total phenolic content

Both cocoa and cinnamon contain polyphenols. The major polyphenol present in dark chocolate is flavanols, such as epicatechin, catechin, and procyanidin (Beckett 2008). The phenolic compounds contained in cinnamon are cineole, terpineol, cinnamyl alcohol, cinnamyl acetate, eugenol, methyl eugenol, and linalool. Vanillic acid, gallic acid, *p*-coumaric acid, *p*-hydroxybenzoic acid, and *p*-hydroxybenzaldehyde are polyphenol constituents of cinnamon. If cocoa and cinnamon are combined, the total phenol content of the final product will be increased (Muhammad and Dewettinck 2017).

The Folin-Ciocalteu method used to determine the total phenol content is easy, rapid, and the most common method used in dark chocolate and cinnamon extract studies (Ervina et al. 2016; Muhammad and Dewettinck 2017; Muhammad et al. 2017, 2018). Table 4 shows that variation of cinnamon bark oleoresin microcapsule addition resulted in a significant difference in dark chocolate bars' total phenol content in both solvents. The total phenol content increased with the increase in the cinnamon bark oleoresin microcapsule concentration, and the chocolate bar F3 contained the highest total phenol content. The total phenol content of the acetone:aquades:acetic acid extract increased to four times higher than that of the methanolic extract. This result is consistent with Muhammad et al. (2018). The addition of 2% lyophilized colloidal nanoparticles containing cinnamon extract resulted in a total phenol content that was approximately two times higher than that of the control chocolate.

The acetone:aquades:acetic acid solvent gave a higher total phenol content because acetone and cinnamaldehyde have the same polarity. Based on the PubChem web-database (2018), the topological polar surface area (TPSA) of acetone and cinnamaldehyde is 17,1 A^2, while the TPSA for methanol is 20,2 A^2. Thus, the hydroxyl group of cinnamaldehyde, which is a major polyphenol compound found in cinnamon bark (Başer and Buchbauer 2010), bonded to the phenyl ring of the acetone:aquades:acetic acid solvent during the Folin-Ciocalteu assay and gave a higher calculation result.

Antioxidant activity

Antioxidant activity is presented as the DPPH IC50 value, which is shown in Table 4. DPPH, along with FRAP and ORAC, is the most common type of antioxidant assay. It is usually used in chocolate- and cinnamon-related studies (Ervina et al. 2016; Muhammad and Dewettinck 2017; Muhammad et al. 2017, 2018). DPPH is a rapid assay that is easy to perform. The Folin-Ciocalteu method is more correlated with DPPH and FRAP than electron transfer by a hydrogen donor (Boeing et al. 2014; Muhammad et al. 2017).

The addition of cinnamon bark oleoresin microcapsules led to a significant difference in antioxidant activity compared to the dark chocolate control. The higher the concentration of added cinnamon bark oleoresin microcapsules, the lower the concentration of the chocolate bar needed to scavenge the 50% free radicals of DPPH. This result is similar to Albak and Tekin (2015), and the active compound in cinnamon play a role in increasing the antioxidant activity of the dark chocolate bar.

All types of polyphenols are antioxidants, including flavonoids, flavonols (catechin and epicatechin), procyanidins, anthocyanidins, flavonol in cocoa (Beckett

2008), eugenol, linalool, and terpineol in cinnamon (Ervina et al. 2016; Muhammad and Dewettinck 2017). Methylxanthines, which are theobromine, caffeine, and theophylline in cocoa, are also antioxidants (Franco et al. 2013). The major compound of *Cinnamomum* sp. bark is the antioxidant cinnamaldehyde, which reaches 70% (Başer and Buchbauer 2010).

The use of different solvents in the extractions gave different IC50 values. The IC50 value for the acetone:aquades:acetic acid extract was lower than the methanolic extract, so its antioxidant activity was higher. Even so, all of the samples were classified as super weak antioxidants. According to the antioxidant classification by Molyneux (2004), a super potent antioxidant has IC50 < 50 ppm, while strong is 50–100 ppm, middle is 10–150 ppm, weak is 150–200 ppm, and super weak is > 200 ppm. The IC50 value of the acetone:aquades:acetic acid extract from dark chocolate bars with the addition of the cinnamon bark oleoresin microcapsules was 200 ppm, which is considered weak. The antioxidant content in products is not a constant value; it differs depending on many aspects, including the condition, processing, or assay method of the materials (Beckett 2008; Muhammad and Dewettinck 2017). The result of the antioxidant activity IC50 evaluation was linear with the total phenol and GC–MS evaluations. Previous studies by Muhammad et al. (2017) showed the same result: the antioxidant activity that was evaluated was positively correlated with the total phenol content.

GC–MS detection

According to Table 5, all of the compounds detected contain cacao and its processing products. The compounds found in all formulas were vanillin, methylxanthines (caffeine and theobromine), fatty acids (palmitic acid and oleic acid), and tocopherols. Franco et al. (2013) stated that the methylxanthines present in cocoa are caffeine, theobromine, and theophylline. The major methylxanthines in cocoa are theobromine and caffeine at lower concentrations (Beckett 2008; Franco et al. 2013). The cocoa bean primarily contains cocoa fat, which is composed of palmitic acid, stearic acid, and oleic acid (Beckett 2008).

According to Djafar and Redha (2012) and Boeing et al. (2014), different solvents will give different assay results, and the solvent used strongly determines the solubility of the bioactive compound. Cinnamaldehyde was not found in the GC–MS evaluation using the methanolic extract, so other solvents, such as acetone:aquades:acetic acid, were used to extract the defatted chocolate. As shown in Table 5, the cinnamaldehyde content of the acetone:aquades:acetic acid extract was 56.3362%. In addition to cinnamaldehyde, theobromine and caffeine were also detected using acetone:aquades:acetic acid, but the percentage was different than the methanolic extract because acetone was probably not the best solvent for methylxanthine. As previously explained, the topological polar surface area of acetone and cinnamaldehyde is exactly the same (PubChem web-database 2018) and was suspected to be the main reason for the solvent and compound interaction.

One of the functional food criteria, according to BPOM RI Regulation No. HK 00.05.52.0685 (2005), is the antioxidant content of the product. GC–MS detection showed that chocolate bars with the addition of the cinnamon bark oleoresin microcapsules contained methylxanthine, vanillin, tocopherol, and cinnamaldehyde as antioxidants. Among the detected antioxidants, tocopherol is the only compound that is already regulated according to its nutrient label by the FDA (2017).

As shown in Table 6, β- and γ-tocopherol were converted to α- tocopherol based on EFSA (2008), so it could be claimed to be the source of regulation. The vitamin E and α- tocopherol contents did not exceed the limit of the BPOM Regulation No. HK. 00. 05. 23. 3644 in 2004. The concentration of α- tocopherol in dark chocolate bars was higher than in the control and exceeded ≥ 100% of the RDI for children (4 years old) and adults (FDA 2017). Therefore, dark chocolate bars with the addition of the cinnamon bark oleoresin microcapsules had a high potency of vitamin E and fulfilled the antioxidant need of adults and children.

Determination of the best formula

The best dark chocolate bar formula was determined by a model weighting test (Sullivan et al. 2015). The parameters used for determining the best dark chocolate bar formula were the attribute, L* and hue angle, hardness (N), methylxanthine and tocopherol contents, moisture content (%), total phenol content (%), and antioxidant activity IC50 (ppm). Each parameter was given a weight from 0 to 1 according to its effect on sample quality. All parameters had the same effect on dark chocolate bar quality, so all parameters were weighted as 1. F3 had the highest total score (0.8724), followed by F1(0.3794) and F2 (0.1602). Therefore F3, which had an 8% addition of cinnamon bark oleoresin microcapsules, was the best formula for a dark chocolate bar.

Further research may evaluate the effect of increased microcapsule addition (> 8%) to dark chocolate or a higher oleoresin concentration added to microcapsules for later addition to dark chocolate. A higher concentration of cinnamon microcapsules increased the total phenolic content and antioxidant activity of dark chocolate bars (Albak and Tekin 2015; Muhammad and Dewettinck 2017) and also

Table 5 GC–MS detection of dark chocolate bar with addition of cinnamon bark oleoresin microcapsule

No.	Compounds	Content (%)				
		Met				AAA
		C	F1	F2	F3	F3
Methylxanthines						
1.	Theobromine	16.458	25.050	17.342	33.879	11.993
2.	Caffeine	6.439	11.272	6.719	10.879	31.671
Aldehyde						
3.	Cinnamaldehyde	–	–	–	–	56.336
4.	Benzaldehyde, 4-hydroxy-3-methoxy (vanillin)	2.735	4.748	3.184	2.490	–
Fatty acids						
5.	Palmitic acid	26.600	26.795	18.237	1.325	–
6.	Oleic acid	21.685	11.789	44.40	14.667	–
7.	Linoleic acid	–	–	–	31.106	–
8.	Lauric acid (dodecanoic acid)	–	–	0.795	2.280	–
9.	Trans-oleic acid (elaidic acid)	5.410	11.017	–	–	–
Tocopherols						
10.	β-tocopherol	1.618	3.094	–	3.376	–
11.	γ- tocopherol	–	–	2.543	–	–
Phytosterols						
12.	Campesterol	–	–	3.151	–	–
13.	β-sitosterol	–	–	3.632	–	–
14.	γ-sitosterol	–	3.808	–	–	–
Hidrocarbons						
15.	Pentadecane	3.402	2.426	–	–	–
16.	Heptadecane-8-carbonic acid-1-	0.698	–	–	–	–
Ester						
17.	Ethyl cinnamate	1.471	–	–	–	–
18.	Ethyl p-methoxy cinnamate	5.426	–	–	–	–
Amide						
19.	Palmitic amide	0.497	–	–	–	–

Met, methanol; AAA, acetone:aquades:acetic acid

Cinnamon bark oleoresin microcapsule addition C = 0%, F1 = 4%, F2 = 6%, F3 = 8%

Table 6 Tocopherol content of dark chocolate bar with addition of cinnamon bark oleoresin microcapsule (F3, Met) and claims based on regulations (BPOM 2004; FDA 2017)

Formula	Tocopherol content[a] (%)			α-tocopherol[b]		FDA RDI (mg)	BPOM Maximum intake (IU)	Claim
	β	γ	mg	mg	IU			
C	1.618		113.232	56.616	84.358	15	400	High-potency antioxidant[c], not exceed
F1	3.094		216.580	108.290	161.352			
F2		2.543	177.989	44.497	66.301			
F3	3.376		236.299	118.150	176.043			

Met, methanol; AAA, acetone:aquades:acetic acid

[a]Content per 1 chocolate block (7 g) which identified in vitro using GC–MS assay

[b]1 mg d-α-tocopherol = 1,49 IU, 1 mg d-α-tocopherol = 2 mg d-β-tocopherol = 4 mg d-γ- tocopherol

[c]Contain ≥ 100% of RDI vitamin E (tocopherol) for adults and children (4 years old)

led to more compounds in GC–MS detection (Beckett 2008; Franco et al. 2013; Ervina et al. 2016; Muhammad and Dewettinck 2017). The texture and colour of dark chocolate may be affected as well. However, the main concern is surely acceptability to consumers. A sensory test using a series of formulas higher than 8% needs to be performed to determine the threshold of flavour rejection. Thus, we can determine the optimum formula that is desirable and gives higher functional effects.

Based on texture analysis, adding more microcapsules will lead to compactness (Midaryanto and Yuwono 2014) and give a harder texture, which affects consumer acceptance. An alternative to adding a smaller amount of microcapsules is increasing the oleoresin concentration in the microcapsules. An increase in the cinnamon oleoresin concentration will increase the functional properties of dark chocolate, as shown by Albak and Tekin (2015). Nevertheless, this alternative also leads to other changes. An increase in the oleoresin concentration for the same shell material formulation can increase the interaction of cinnamaldehyde with amino acids (López-Mata et al. 2015). This interaction will lead to oleoresin diffusion outside of the shell materials, which affects colour, sensory acceptability, and the loss of volatile bioactive compounds. Thus, studies to define the best microencapsulation formula need to be performed first.

Conclusion

Panellist preference, the moisture content, and the chromatic colour (hue angle) of dark chocolates bar were not significantly affected by the variation of the added cinnamon bark oleoresin microcapsules. The addition of oleoresin microcapsules significantly affected the lightness (L*), texture, total phenol content, and antioxidant activity IC50. The higher the amount of added cinnamon bark oleoresin microcapsules, the higher the total phenol content and antioxidant activity IC50 of the dark chocolate bars. The acetone:aquades:acetic acid extract led a higher total phenol content and antioxidant activity than the methanolic extract. The GC–MS results of the methanolic extract showed the presence of methylxanthines, aldehydes, tocopherols, fatty acids, phytosterols, hydrocarbons, esters, and amides, while analysis of the acetone:aquades:acetic acid extract showed the presence of cinnamaldehyde and methylxanthines. The best formula for a dark chocolate bar with the addition of cinnamon bark oleoresin microcapsules is F3 (8%), which also contains the high potency antioxidant tocopherol.

Acknowledgements The authors would like to thank Universitas Sebelas Maret (UNS), Indonesia for funding this research under the PNBP Research Grant Scheme 2018 (Nomor 543/UN27.21/PP/2018).

References

Afoakwa E (2010) Chocolate science and technology. Wiley Blackwell, Oxford

Albak F, Tekin AR (2015) Effect of cinnamon powder addition during conching on the flavour of dark chocolate mass. J Food Sci Technol 52:1960–1970. https://doi.org/10.1007/s13197-013-1217-2

Başer KHC, Buchbauer G (2010) Handbook of essential oils: science, technology, and applications, 2nd edn. CRC, Boca Raton

Beckett ST (2008) The science of chocolate, 2nd edn. RSC, Cambridge

Boeing JS, Barizão EO, Silva BC, Montanher PF, Almeida VC, Visentainer JV (2014) Evaluation of solvent effect on the extraction of phenolic compounds and antioxidant capacities from the berries: application of principal component analysis. Chem Cent J 8:48. https://doi.org/10.1186/s13065-014-0048-1

BPOM (2004) Peraturan kepala badan pengawas obat dan makanan republik indonesia hk 00.05.23.3644. BPOM RI, Jakarta

Brunetto MDR, Cayama YD, Gutiérrez L, Roa SC, Méndez YC, Gallignani M, Zambrano A, Gómez A, Ramos G (2009) Headspace gas chromatography-mass spectrometry determination of alkylpyrazines in cocoa liquor samples. J Food Chem 112:253–257. https://doi.org/10.1016/j.foodchem.2008.05.082

Chen P, Sun J, Ford P (2014) Differentiation of the four major species of cinnamons (*C. burmannii*, *C. verum*, *C. cassia*, and *C. loureiroi*) using a flow injection mass spectrometric (FIMS) fingerprinting method. J Agric Food Chem 62:2516–2521. https://doi.org/10.1021/jf405580c

Direktorat Jenderal Perkebunan Indonesia (2016) Statistik perkebunan indonesia 2015–2017. Sek Dir Jen Perkebunan, Jakarta

Djafar F, Redha F (2012) Karakterisasi dan modifikasi sifat fungsional kayu manis dalam produk pangan. J Has Pertan Ind 25:18–25

Dwijatmoko MI, Praseptiangga D, Muhammad DRA (2016) Effect of cinnamon essential oils addition in the sensory attributes of dark chocolate. Nusant Biosci 8:301–305. https://doi.org/10.13057/nusbiosci/n080227

Ervina M, Nawu YE, Esar SY (2016) Comparison of in vitro antioxidant activity of infusion, extract, and fractions of indonesian cinnamon (*Cinnamomum burmannii*) bark. Int Food Res J 23(3):1346–1350

European Food Safety Authority (2008) Opinion on mixed tocopherols, tocotrienol tocopherol, and tocotrionols as sources for vitamin E added as a nutritional substance in food supplements. EFSA J 640:1-34. https://doi.org/10.2903/j.efsa.2008.640

FAO-AGST (2002) Ginger: post harvest operations. UN FAO, Rome

FAOSTAT (2016) Cinnamon (canela). FAO website. http://www.fao.org/faostat/en/#data/TP. Accessed 8 Sept 2018

FDA (2017) 21CFR101.9 nutrient labelling of food. FDA access. http://ww.accessdata.fda.gov/scripts/cdrh/cfdocs/cfcfr/CFRSearch.cfm?fr=101.9. Accessed 18 Apr 2018

Franco R, Onatibia-Astibia A, Matinez-Pinilla E (2013) Health benefits of methylxanthines in cacao and chocolate. Nutrients 5:4159–4161. https://doi.org/10.3390/nu5104159

Gao L, Ren W, Li F, Cheng HM (2008) Total colour difference for rapid and accurate identification of graphene. ACS Nano 2:1625–1633. https://doi.org/10.1021/nn800307s

Goncalves EV, Lannes SCDS (2010) Chocolate rheology. Cienc Tecnol de Alimentos Campinas 30:845–851. https://doi.org/10.1590/S0101-20612010000400002

Ilmi A, Praseptiangga D, Muhammad DRA (2016) Sensory attributes and preliminary characterization of milk chocolate bar enriched with cinnamon essential oil. IOP Conf Ser Mater Sci Eng 193:1–7. https://doi.org/10.1088/1757-899X/193/1/012031

International Cocoa Organization (2017) Quarterly bulletin of cocoa statistics XLVIII no. 1 cocoa year 2016/17. ICCO, Abidjan

Irfiana D, Utami R, Khasanah LU, Manuhara GJ (2017) Preservation effect of two-stage cinnamon bark (*Cinnamomum burmannii*) oleoresin microcapsules on vacuum-packed ground beef during refrigerated storage. IOP Conf Ser Mater Sci Eng 193:1–7. https://doi.org/10.1088/1757-899X/193/1/012026

Kania W, Andriani MAM, Siswanti S (2015) Pengaruh variasi rasio bahan pengikat terhadap karakteristik fisik dan kimia granul minuman fungsional instan kecambah kacang komak (*Lablab purpureus* (L.) sweet). J Tek Pangan 4:16–24

Khasanah LU, Anandito RBK, Utami R, Kusumaningrum P, Waningsih M (2014) Reduksi sisa pelarut etanol oleoresin kayu manis (*Cinnamomum burmannii*). J Teknol Ind Pertan 24:53–60

Khasanah LU, Anandhito BK, Rachmawaty T, Utami R, Manuhara GJ (2015) Pengaruh rasio bahan penyalut maltodekstrin, gum arab, dan susu skim terhadap karakteristik fisik dan kimia mikrokapsul oleoresin dan daun kayu manis (*Cinnamomum burmanii*). Agritech 35:415–421. https://doi.org/10.22146/agritech.9325

Khasanah LU, Anandito BK, Uyun Q, Utami R, Manuhara GJ (2017) Optimasi proses ekstraksi dan karakterisasi oleoresin daun kayu manis (*Cinnamomum burmanii*) dua tahap. Indones J Essent Oil 2:20–28

López-Mata MA, Ruiz-Cruz S, Silva-Beltrán NP, Ornelas-Paz JDJ, Ocaño-Higuera VM, Rodríguez-Félix F, Cira-Cháves LA, Del-Toro-Sánchez CL, Shirai K (2015) Physicochemical and antioxidant properties of chitosan films incorporated with cinnamon oil. Int J Polym Sci. https://doi.org/10.1155/2015/974506

Midaryanto DN, Yuwono SS (2014) Penentuan atribut mutu tekstur untuk direkomendasikan sebagai syarat tambahan dalam standar nasional indonesia. J Pangan dan Agroind 2:259–267

Molyneux P (2004) The Use of the stable free radical diphenylpicrylhydrazyl (DPPH) for estimating antioxidant activity. Songklanakarin J Sci Technol 26:211–219

Muhammad DRA, Dewettinck K (2017) Cinnamon and its derivatives as the potential ingredients in the functional food-a review. Int J Food Prop. https://doi.org/10.1080/10942912.2017.1369102

Muhammad DRA, Praseptiangga D, Van de Walle D, Dewettinck K (2017) Interaction between natural antioxidants derived from cinnamon and cocoa in the binary and complex mixture. Food Chem 231:356–364. https://doi.org/10.1016/j.foodchem.2017.03.128

Muhammad DRA, Saputro AD, Rottiers H, Van de Walle D, Dewettinck K (2018) Physicochemical properties and antioxidant activities of chocolates enriched with engineered cinnamon nanoparticles. Eur Food Res Technol 244:1185–1202. https://doi.org/10.1007/s00217-018-3035-2

Murti LW (2012) Pengaruh variasi rasio bahan penyalut gum arab dan maltodekstrin terhadap karakteristik mutu mikroenkapsulan oleoresinkayu manis (Cinnamomum burmannii). Skripsi Jurusan Teknologi Hasil PertanianFakultas Pertanian. Universitas Sebelas Maret, Surakarta, Indonesia

Praseptiangga D, Nabila Y, Muhammad DRA (2018) Kajian tingkat penerimaan panelis pada dark chocolate bar dengan penambahan bubuk kayu manis (*Cinnamomum burmanii*). Caraka Tani J Sustain Agric 33:78–88. https://doi.org/10.20961/carakatani.v33i1.19582

Proestos C, Komaitis M (2013) Analysis of naturally occurring phenolic compounds in aromatic plants by RP–HPLC coupled to diode array detector (DAD) and GC–MS after silylation. Foods 2:90–99. https://doi.org/10.3390/foods2010090

PubChem (2018) Acetone, cinnamaldehyde, methanol. PubChem. https://pubchem.ncbi.nlm.nih.gov/. Accessed 22 May 2018

Rasuluntari IN, Muhammad DRA, Praseptiangga D (2016) Panellist acceptance level on milk chocolate with cinnamon (*Cinnamomum burmannii*) powder addition. Nusant Biosci 8:297–300. https://doi.org/10.13057/nusbiosci/n080226

Renard CMGC, Maingonnat JF (2012) Thermal processing of fruit and fruit juices. In: Sun DW (ed) Thermal food processing: new technologies and quality issues, 2nd edn. CRC, Boca Raton

Sullivan WG, Wicks EM, Koelling CP (2015) Engineering economy. Pearson Higher Education Inc, New Jersey