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The Process Optimization Of Microwave Assisted Extraction On Cinnamomum Verum J. Presl. Extraction Yield And Comparative Of Chemical Compositions To Supercritical Fluid Extraction And Hydrodistillation

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Abstract

In this present work, the optimization of microwave assisted extraction (MAE) for cinnamon (Cinnamomum verum J.Presl.) was investigated to compare the extraction yields and chemical compositions with hydrodistillation (HD) and supercritical fluid extraction (SFE). The effects of different parameters (microwave power, extraction time and liquid to solid ratio) were investigated to obtain the optimum yield from MAE. Response surface method (RSM) using Box-Behnken design (BBD) was deployed for the design of experiment and optimization for MAE. The chemical compositions of cinnamon essential oils were analyzed by gas chromatography-mass spectrometry (GC-MS). From the experimental result, the extraction yields of HD, MAE and SFE were 2.13%, 2.86% and 6.83% respectively. However, MAE shown better result on extraction time than HD and SFE. From RSM result, the highest yield of MAE was obtained by microwave power (662 W), extraction time (36.8 min) and solid to liquid ratio (100g/513mL). The results from GC-MS presented that MAE was shown better result on many terpene contents than HD and SFE. Cinnamaldehyde and cinnamyl acetate were detected from MAE higher than SFE but lower than HD. However, methoxycinnamaldehyde was detected from MAE higher than HD and SFE significantly.

Keywords: Microwave assisted extraction, cinnamon, critical fluid extraction, response surface method, cinnamaldehyde, cinnamyl acetate

Introduction

The utilizations of herbs as condiments, flavoring agents or medicines are integrated into many industrials around the world. Essential oils extracted from herbs are well known that rich of biochemical compositions, aromatic compounds and antioxidant. Cinnamon is one of the most famous herb that utilized in many products such as aroma oil, cosmetics and pharmacology [1,2]. Cinnamon is widely cultivated in many countries such as India, China, Portugal, German and including Southeast Asia. The different parts of cinnamon such as bark, leaf and root are always utilized as traditional medicine due to its chemical compositions and unique aromatic values [3]. In many regions of Southeast Asia, including Thailand, cinnamon is one of the local plants that cultivated to support medicine, food and nutrition industry. Cinnamons that have growth in Thailand are classified into five main groups which are Cinnamomum verum J.Presl., Cinnamomum cassia (L.) J.Presl., Cinnamomum

loureiroi Nees, Cinnamomum burmanni (Nees & T.Nees) Blume and Cinnamomum bejolghota (Buch.-Ham.) Sweet [4]. However, the famous of cinnamon species that widely cultivated in Thailand are Cinnamomum verum J.Presl. and Cinnamomum burmanni (Nees & T.Nees) Blume.

In recent years, MAE was deployed to extract essential oils from many plant samples to investigate the optimization of process parameters and efficiency by compare with different methods. Extraction yield and chemical compositions such as polysaccharides, pectin and other antioxidants were extracted by MAE [5,6,7]. It was indicated that the important process parameters such as microwave power, extraction time and solvent ratio were resulted directly to extraction yield and chemical compositions content. The essential oils from dried cinnamon bark (Cinnamomum cassia) were extracted by hydrodistillation (HD) and microwave-assisted extraction (MAE) to investigate the morphological changing and its chemical compositions [1]. From the scanning electron microscope (SEM) result, the microstructures of cinnamon by HD shown higher aggressive disruption and mechanical strain than MAE. It may be caused of the explosive disruption of oil gland and led to lower rate of some chemical compositions when compared with MAE. The extraction oil from cinnamon leaves was also extracted with two processes combination between enzymolysis pretreatment and MAE (EP-MAE). The process parameters (microwave power, water to liquid ratio, enzyme amount and time) were investigated to improve the quality of essential oil and extraction yield by compare with HD and MAE [3]. The percentage results of oxygenated compositions from EP-MAE and MAE were higher than HD. It indicated that the heat generation mechanism of microwave also effected to chemical compositions of essential oil. MAE and different types of solvent were also studied for the investigation of cinnamaldehyde and cinnamic acid amounts by compared with reflux extraction (RF) and ultrasonic assisted extraction (UAE) [8]. Cinnamaldehyde and cinnamic are also known as the very important compositions that contain in cinnamon [9,10]. The result indicated that MAE could provide better result for both compositions than HD and UAE. The chemical compositions of essential oils from cinnamon (Cinnamomum cassia Presl) with three different extraction methods were analyzed by gas chromatography-mass spectrometry (GC-MS) [9]. Stream distillation (SD), microwave assisted stream distillation (MASD) and ultrasonic assisted stream distillation (USAD) were deployed to extract essential oils cinnamon samples. The result shown that extraction yield of USAD was higher than SD and MASD. However, MASD presented some of major compositions such as cinnamyl acetate and 2-methoxycinnamaldehyde better than SD and UASD. Furthermore, three extraction methods (soxhlet, MAE and UAE) were also deployed to extract cinnamon sample from India [10]. The GC-MS results also shown cinnamaldehyde and cinnamic acid content of MAE higher than UAE but also lower than soxhlet. However, MAE illustrated the advantages in shorter extraction time, less solvent consumption and energy than soxhlet and UAE.

The essential oils obtained from supercritical fluid extraction (SFE) with different process parameters were also studied to investigate the effect of pressure, temperature and time on extraction yield and chemical compositions [11]. The results shown that the pressure and temperature were directly resulted to the major compositions of the essential oils. SFE is an extraction method that utilizes the mechanism of gas fluid such as carbon dioxide over its critical point [11,12]. SFE is also known as one of green extraction methods that have more advantages such as lower extraction temperature and excellent for nonpolar components [12,13]. Although, the volatile aldehyde such as cinnamaldehyde obtained from SFE presented in desirable rate [11], but on the other hand cinnamyl acetate which is ester was lower than the results from SD and MASD significantly [9]. Nowadays, MAE is also known as one of the green extraction methods due to its lower power

consumption, shorter extraction time and lower amount of solvent when compare with traditional methods [14]. The heat generation mechanism of MAE is derived from two main phenomena which are ionic conduction and dipole rotation. As the orientation of the electric field changes over time, the polar molecules of plants attempt to follow the field by changing their orientation inside material [15]. For this reason, temperature of material is increased with the changing of molecules direction rapidly. For the study of novel extraction method for cinnamon oil, ultrasound-enhanced subcritical water extraction (USWE) was also used to investigation of extraction yield and relative contents of cinnamaldehyde and other compositions [16]. Subcritical water extraction is new technique that deploys water with high temperature and appropriate pressure to maintain liquid state as extraction solvent. Process parameters of USWE (time, temperature and ultrasonic power) were optimized to obtain the optimum oil yield and cinnamaldehyde percent content. However, the results were presented lower cinnamon oil yield and cinnamaldehyde content when compared with SD and MAE.

However, the essential oils from cinnamon were also studied and investigated with various extraction methods as mentioned from previous. The difference of extraction yield and chemical compositions of cinnamon due to its various cultivate areas and extraction methods are still the potential topics. Aims of this study were the optimization of process parameters of microwave assisted extraction on extraction yield and investigation of chemical compositions obtained by three different methods. Essential oils obtained from HD, MAE and SFE were analyzed by GC-MS to identify the chemical compositions. Response surface method (RSM) using Box-Behnken design (BBD) type and analysis of variance (ANOVA) were investigated to optimize the extraction oil yield. Cinnamon (Cinnamomum verum J.Presl) samples were prepared in this study for the experimental procedure and analysis.

MATERIALS AND METHODS

Materials preparation:

The dried cinnamon (Cinnamomum verum J.Presl.) barks were collected from Thaprachan herb company that located in Bangkok, Thailand. The dried cinnamon barks were washed to remove some dirt and dried in hot chamber oven at 50 °C for 3 hours to decrease moisture. After this, the dry cinnamon barks were ground using grinder machine and sieved using sieve shaker machine assembled with a 50 standard mesh size. Prior to experimental, 100 g of the cinnamon bark powder was weighted and kept in refrigerator at 4.0 °C until further process. For HD and MAE, distilled water was mixed with cinnamon power samples at different ratios under experimental design, meanwhile liquid CO_2 was deployed in SFE as solvent.

Hydrodistillation extraction (HD)

An appropriate Clevenger type apparatus with heating mantle was used for the extraction of cinnamon oil. A round bottom flask (1000 mL) was used to contain the cinnamon powder sample and distilled water. The condensing unit of clevenger apparatus was connected to the water chiller that was set cooling temperature at 5.0 °C. In this study, the extraction temperature of HD was set constant at 120.0 °C. The distilled water (600 mL) was mixed with the cinnamon powder and the extraction time for HD was set at 2 hours. The schematic diagram and equipment of HD in this study were shown in Fig 1.

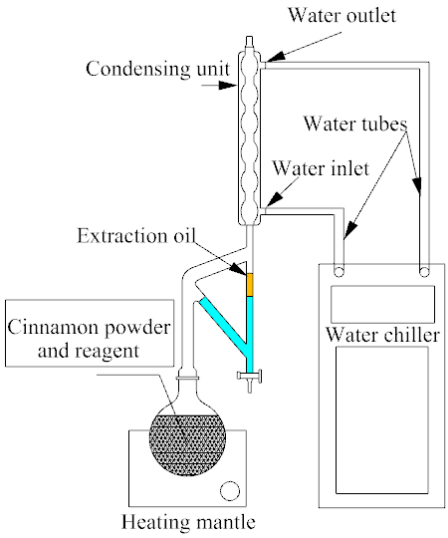


Fig 1. Schematic diagram of essential oil extraction from cinnamon with HD

Microwave-assisted extraction (MAE)

Microwave power generation and control unit were obtained from commercial microwave oven (Model: ER-SM20(W), Toshiba, Thailand) with maximum power at 800 W. Microwave oven chamber was redesigned to increase amount capacity from 20 to 35 liters. The microwave generation unit cover and chamber were fabricated of stainless steel sheet metal (SUS304) with thickness of 1.5 mm. An appropriate clevenger type apparatus with round bottom flask (1000 ml.) was deployed for MAE in this study. Microwave radiation leakage was investigated with microwave leak detector before using. The condensing unit of clevenger apparatus for MAE was connected with water chiller as same as HD. The schematic of MAE in this study was shown in Fig 2. The independent process parameters (microwave power, extraction time and solid/liquid ratio) of MAE with three levels were shown in Table 1. and cinnamon powder (100 g) was used in each of the experimental of MAE.

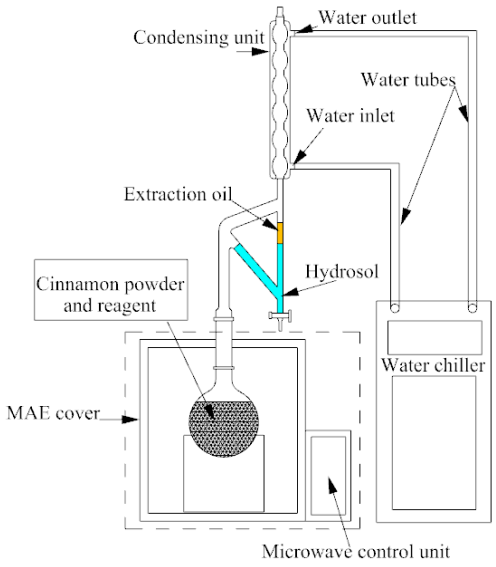


Fig 2. Schematic of essential oil extraction from cinnamon with MAE

Supercritical fluid extraction (SFE)

The extraction was performed using a supercritical CO_2 extraction device (LNCOSE-5, Hefei Linuo Scientific Instrument Co., ltd, China). The diagram in Fig 3. is illustrated the main components and sequence of cinnamon oil extraction process. The separation unit of device is consisted of extractor and two gravimetric separators. The maximum capacity of extractor is approximately 1.5 liters. Cinnamon powder sample (100 g) was loaded in to the container of extractor unit. At the initial stage, CO_2 from storage tanks was loaded directly into filter and kept to storage tank. The filtered CO_2 was fed into mixer unit with high pressure pump. The entrainer pump was responded to improve the efficiency of extraction by mixing homogeneously between plant sample and CO_2. The proper amount of mixing was soaked at steady state within extractor unit for 2 hours and CO_2 was cooled down immediately to 4 °C by a water chiller. The flow rate of CO_2 was set at 6.0 L/h. and temperature of extraction unit was controlled at 45.0 °C by hot water tube around extractor.

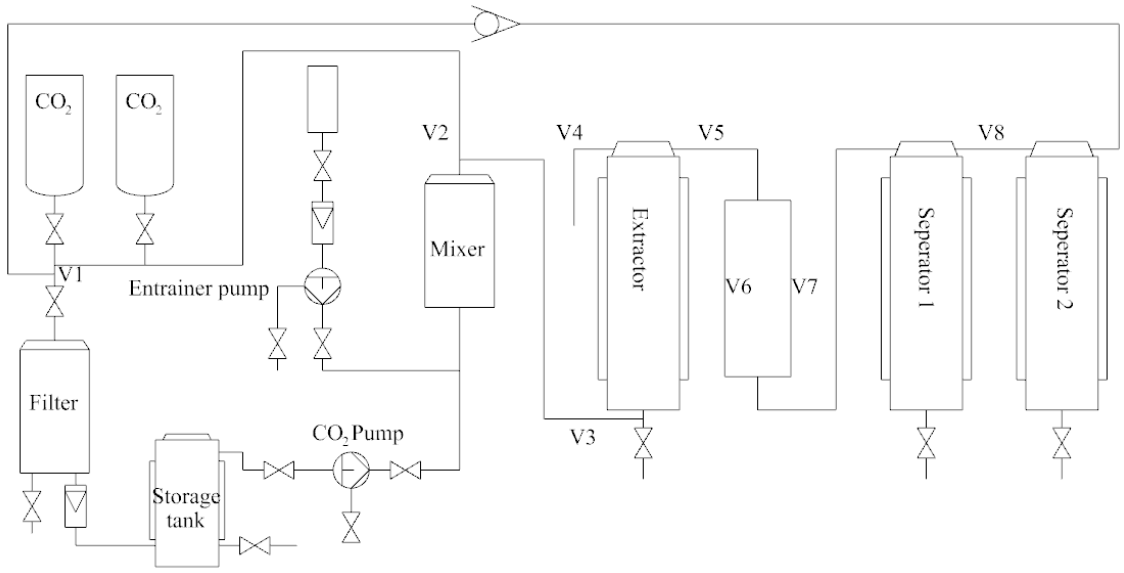


Fig 3. Schematic of essential oil extraction from cinnamon with SFE

The extraction oil yields of cinnamon and sample analysis

All extraction oil yields obtained from HD and MAE were separated from hydrosol and measured weight to calculate the extraction yield. In case of SFE, the extraction oil yields were released from two separators and measured weight. Yield of the essential oils from HD, MAE and SFE were determined triplicate, and the results were presented as an average value. The extraction yield results of HD, MAE and SFE were calculated by the equation as follows (1):

$$\text{Yield \% (w/w)} = \frac{\text{weight of extraction oil (g)}}{\text{weight of cinnamon powder (g)}} \times 100\% \quad (1)$$

In this study, chemical composition of essential oils from HD, MAE and SFE were analyzed by GC-MS. Shimadzu model GCMS-QP2020 was carried out to identify their chemical compositions. DB-WAX column (30 m × 0.25 mm × 0.25 µm) and MSD mass detector (scan at 45-350 m/z) were fitted and assembled into equipment. Helium was chosen as carrier gas to contain collected sample into column. Flow rate of carrier gas was set at constant rate (1.0 mL/min). The collected sample was mixed with dichloromethane (1.0 mg/mL) and injected with a split ratio (1.0 mL/min). The initial temperature of

the oven was set at 60 °C for 1.0 min and increased 2 °C/min until it reached 250 °C for a 5-minute holding time. Data processing and analysis were carried out on LabSolutions DB/CS software.

The process optimization of cinnamon oil yield by MAE

The experimental design for MAE in this study was carried out response surface methodology (RSM) to optimize the optimal essential oil yield from cinnamon. The Design of experiment (DOE) of MAE was designed within Bok-Behnken Design (BBD) with three numeric factors at three levels (-1,0,+1). Three independent variables consisted of microwave power (400, 600 and 800 W), solid/liquid ratio (400, 500 and 600 mL) and extraction time (15, 30 and 45 min). The independent variables and coded setting levels for MAE is shown in Table 1. A total of 15 experiments including 3 center points were designed using BBD as shown in Table 2. The second-order polynomial was used to predict the relationship between process parameters and extraction yield. The quadratic model is expressed by the following Eq. (2).

$$Y = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \beta_{12} X_1 X_2 + \beta_{13} X_1 X_3 + \beta_{23} X_2 X_3 + \beta_{11} X_1^2 + \beta_{22} X_2^2 + \beta_{33} X_3^2 \quad (2)$$

Where Y is the predicted response; β_0 is model constant and; β_1, β_2 and β_3 are linear coefficients; β_{12}, β_{13} and β_{23} are cross-product coefficients; β_{11}, β_{22} and β_{33} are quadratic coefficients and X_1, X_2 and X_3 are independent variables.

Table.1 Independent parameters and coded setting levels for MAE

Independent parameters	Code setting levels		
	-1	0	1
Microwave power (W) (X1)	400	600	800
Microwave time (min) (X2)	15	30	45
Liquid to solid ratio (mL) (X3)	400	500	600

Table 2. Experimental design matrix with BBD and response values

No.	Code setting level			Actual setting level			%Yield	
	X1	X2	X3	X1 (W)	X2 (min)	X3 (ml.)	Predicted	Actual
1	1	0	1	800	30	600	2.36	2.37
2	0	1	1	600	45	600	2.47	2.43
3	0	0	0	600	30	500	2.83	2.86
4	0	0	0	600	30	500	2.83	2.78
5	0	-1	1	600	15	600	1.78	1.86

6	-1	0	-1	400	30	400	1.45	1.44
7	1	1	0	800	45	500	2.61	2.63
8	0	1	-1	600	45	400	2.33	2.25
9	0	-1	-1	600	15	400	1.33	1.37
10	-1	1	0	400	45	500	1.95	2.04
11	1	0	-1	800	30	400	2.11	2.16
12	-1	-1	0	400	15	500	1.15	1.13
13	1	-1	0	800	15	500	1.73	1.64
14	0	0	0	600	30	500	2.83	2.33
15	-1	0	1	400	30	600	1.78	1.91

Statistical Data Analysis

The BBD experimental design, multiple linear regression and RSM in this study were performed by using Minitab v.19.1 (trial version). The experimental results were analyzed by analysis of variance (ANOVA) with the significance levels of 0.5. The satisfactory of the models results were analyzed and evaluated by the coefficient of multiple determination (R^2) and p-values. The contour and surface plots were calculated and plotted within the Minitab software to illustrate the relationship between extraction yield and process parameters.

RESULT AND DISCUSSION

Comparison of extraction yields between HD, MAE and SFE

The results of extraction yield from MAE were shown in Table 2. The highest yield obtained from MAE was 2.86 % at microwave power (800 W), extraction time (30 min) and solid/liquid ratio (100 g/600 mL). Meanwhile, the lowest of extraction yield from MAE was 1.67 % at microwave power (600 W), extraction time (15 min) and solid/liquid ratio (100 g/400 mL). The highest yield from MAE that obtained in this study was slightly higher than previous report [10]. Moreover, the extraction time was shorter than that among 60 min. The extraction yield obtained from HD in this study was 2.13 % that lower than the highest result from MAE among 0.73 %. Meanwhile, the result of extraction yield from SFE was 6.83 % that higher than HD and MAE significantly. However, the highest result of extraction yield that obtained from SFE in this study was slightly lower than previous report [20] among 1.17 %. The comparison of extraction yields between HD, MAE and SFE are shown in Figure 4.

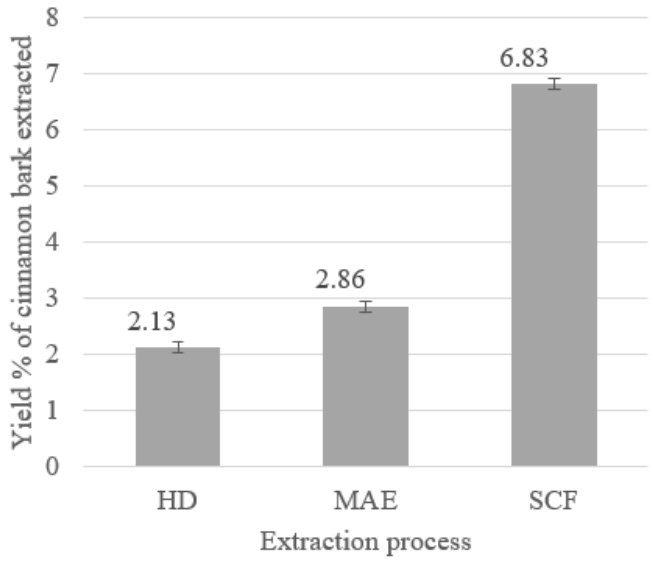


Figure 4. Comparison of extraction yields between extraction methods

Optimization of extraction yield and analysis of variance (ANOVA)

Analysis of variance (ANOVA) of the quadratic regression model are shown in Table 3. The values of determination coefficient (R^2) and the adjusted determination coefficient (R^2_{Adj}) were 0.990 and 0.974 respectively. The high degree of both values indicated a significant relationship between the observed and predicted results [5, 7]. Moreover, the high degree of determination coefficient ($R^2 > 0.95$) from the result indicated a strong link between second-order response surface model and observed data. Meanwhile, p-value indicated the significance of model fitness. From the result in Table 3, the p-value of the model was 0.0005 that indicated extremely significant of the model. Moreover, the lack-of-fit of the model was also used to indicate the connection to the experimental data. The lack-of-fit of the result was 0.125, indicating that it was insignificant relative to the pure error ($p > 0.05$).

From ANOVA results in Table 3, linear (X1, X2 and X3) and square (X1*X, X2*X2 and X3*X3) coefficients were extremely significant (p-value < 0.001) and recommended to significantly affect the extraction yield of cinnamon. All Interactions (X1*X2, X1*X3 and X2*X3) coefficients were not significant (p-value < 0.05). The model of regression equation in the coded unit was derived as follows (3):

$$\text{Yield \%} = 2.0967 + 0.2875X_1 + 0.2912X_2 + 0.1263X_3 - 0.0833X_1X_1 - 0.1608X_2X_2 + 0.1992X_3X_3 - 0.0275X_1X_2 + 0.2725X_1X_3 - 0.0350X_2X_3 \quad (3)$$

where X_1, X_2 and X_3 are the coded process variables for microwave power, extraction time and solid-to-liquid ratio respectively

Table 3. ANOVA for response surface of MAE

Source	DF	Adj SS	Adj MS	F-Value	P-Value	Significant
Model	9	4.355	0.484	59.23	0.000	***
Linear	3	2.330	0.777	95.10	0.000	***
A	1	0.756	0.756	92.61	0.000	***
B	1	1.403	1.403	171.74	0.000	***

C	1	0.171	0.171	20.95	0.006	**
Square	3	1.997	0.666	81.49	0.000	***
A*A	1	0.959	0.959	117.38	0.000	***
B*B	1	0.771	0.771	94.44	0.000	***
C*C	1	0.568	0.568	69.49	0.000	***
2-Way Interaction	3	0.027	0.009	1.11	0.427	
A*B	1	0.002	0.002	0.20	0.677	
A*C	1	0.002	0.002	0.20	0.677	
B*C	1	0.024	0.024	2.94	0.147	
Error	5	0.041	0.008			
Lack-of-Fit	3	0.037	0.012	7.19	0.125	
Pure Error	2	0.003	0.002			
Total	14	4.395				

R^2 = 0.990, R^2_{Adj} = 0.974, ***($p < 0.001$); **($p < 0.01$); *($p < 0.05$)

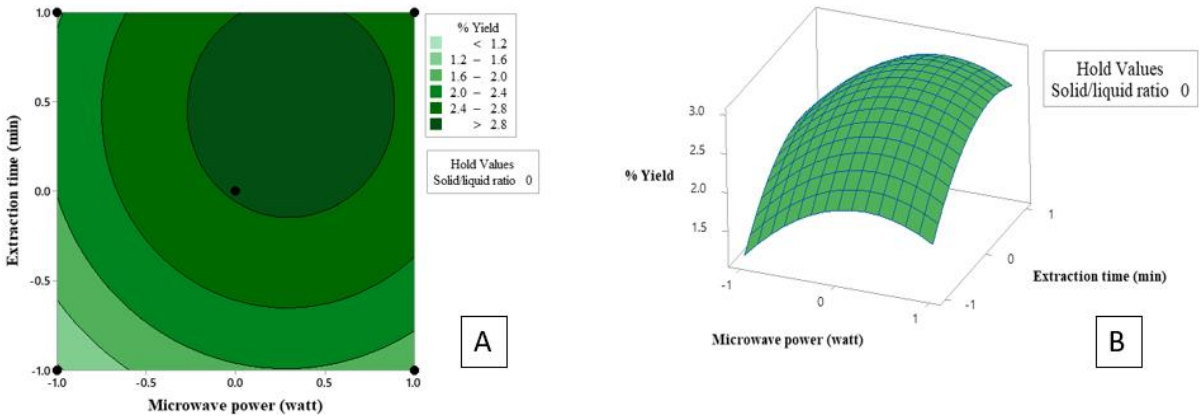
Analysis of response surface method on MAE process parameters

The predictive and actual results of essential oil that obtained from RSM and BBD were shown in Table 2. The interaction between process parameters of MAE (microwave power, extraction time and solid/liquid ratio) on extraction yields were analyzed by RSM. The contour and response surface plots were analyzed to illustrate the relationships between process parameters and response value as shown in Fig 5. The highest yield was 2.86 % that obtained from the experimental run no. 3 and the lowest yield was 1.13% that obtained from run no. 14. In term of the interaction between microwave power and extraction time, the extraction yield increased significantly as the increasing of microwave power from 400 to 600 W. Due to the mechanism of heat generation from microwave irradiation, the temperature of aqueous phase was heated up with the reasons of dipole rotation and ionic conduction [5,6]. From that reasons, the high level of microwave power can lead to the greater temperature at shorter time when compare with the lower level. Moreover, the determination of microwave power level also could have an effect on the mass transfer of microstructures of plant samples and the viscosity rate of solvent. For the further, the morphological of microstructures were more ruptured and exposed due to the high levels of microwave power as the mentions from previous studies [7,22]. The interaction between microwave power and extraction time on the extraction yield of cinnamon are shown in Fig 5(A). and 5(B). The extraction yield of cinnamon was also increased with the increasing of extraction time. At the lowest extraction time, the temperature of aqueous phase might not reach the appropriate boiling point. Hence, the mass transfer of microstructure and the viscosity rate of extraction process could not reach the appropriate proportion to obtain the optimum yield at short extraction time. However, the extraction yield was decreased slightly at the highest microwave power and extraction time. The very high temperature of the extraction process as the results of very high microwave power and longer extraction time could lead to the degradation of cinnamon. Due to the thermo-sensitive circumstance of material, many previous studies also reported the resulting in declined extraction yield as the result of higher temperature and longer time [5,22,24].

In case of the interaction between microwave power and solid/liquid ratio, the highest and lowest yield were amount 2.75% and 1.5 % respectively. The lowest extraction yield obtained from low level of microwave power and solid/liquid ratio. The effects of different distilled water ratio to

cinnamon powder were considered as the essential oil carrier and the prevention of raw material thermal degradation [24]. Due to smaller amount of distilled water ratio, the viscosity rate was higher than lager amount obviously. It may be cause of efficiency decreasing to the carrier of essential oil during extraction process. The extraction oil yield increased with the increasing of solid/liquid ratio as shown in Fig 5(C) and 5(D). The extraction yield was increased significantly with the increasing of microwave power. This indicated that the high level of microwave power could reach the boiling point of the immersed cinnamon better than low level. However, the extraction yield was slightly decreased at the highest level of microwave power and solid/liquid ratio. At the very high temperature as the result of the microwave power increasing, this may be causes of process efficiency decreasing due to plant sample degradation and the burning of immersed cinnamon. Due to the mechanism of heat generation with microwave irradiation that mention above, the immersed cinnamon with the very high level of microwave power could absorb excessive microwave irradiation and reached to the failure form even at the high amount of distilled water. Hence, the extraction yield of cinnamon was decreased with the excessive microwave power level as mention in previous report [1,25].

The interaction between extraction time and solid/liquid ratio on extraction yield are shown in Fig 5(F) and 5(E). The very short of extraction time also shown the low level of extraction yield. Due to the absorption of microwave irradiation of immersed cinnamon, it could not reach the expected efficiency at very short time. Although, the shortest time of MAE in this study was enough to reach the boiling point of the infuse sample. Nevertheless, the extraction time at 15 min could not approach the optimum efficiency time to carry out the essential oil from the immersed cinnamon. Meanwhile, solid/liquid ratio at low amount of distilled water also shown lower extraction yield. However, lower amount of distilled water could approach the boiling point faster than larger amount. In the other hand, the very high viscosity rate and temperature within the immersed cinnamon could be causes of the extraction yield reduction. Although, the extraction yield was increased with the increasing of extraction time and solid/liquid ratio. Nevertheless, the extraction yield decreased at the highest levels of extraction time and solid/liquid ratio. At the longest extraction time, the immersed cinnamon might be the degradation form due to high temperature. Meanwhile, the largest amount of distilled water may employ more microwave energy consumption and extraction time to reach the boiling point of the immersed cinnamon. Due to response surface optimization, MAE conditions for the optimal extraction yield were 2.97 % at microwave power (662 W), extraction time (36.8 min) and solid/liquid ratio (100 g/513 ml).



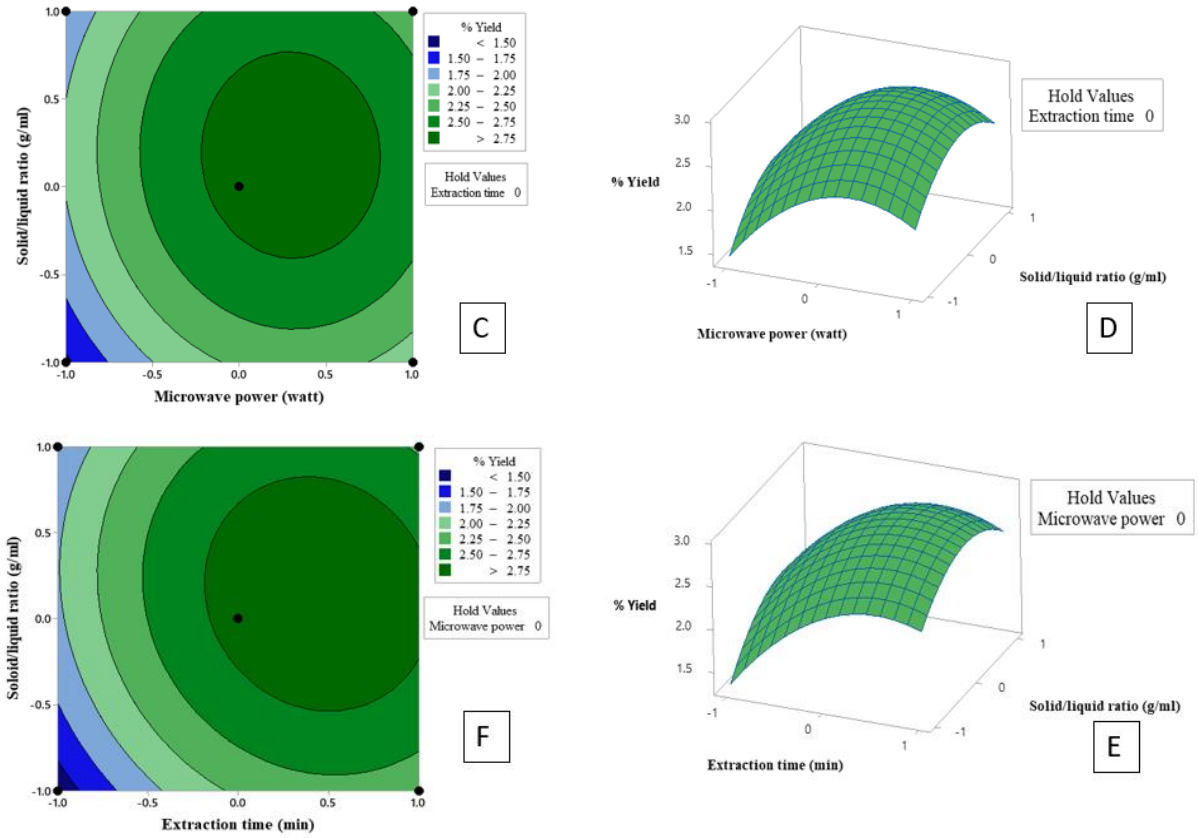


Figure 5. Contour and surface plots of process parameters of MAE on yields

Comparison of chemical compositions between HD, MAE and SFE

The most distinctive composition that was detected in essential oils from HD, MAE and SFE in this study was cinnamaldehyde. It is the very important composition that were detected from cinnamon oils in previous reports [1,8,9]. Cinnamaldehyde is also known as the potential composition to natural food preservative, pharmacology and including dietary supplements. The highest amount of cinnamaldehyde in this study was obtained by HD (72.16%) followed by MAE (53.08%) and SFE (36.78%) respectively. Cinnamyl acetate that is an acetate ester was also detected in HD, MAE and SFE. The percent content of its from HD (10.52%) was slightly higher than MAE (9.57%). Meanwhile, the result of cinnamyl acetate from SFE (3.45%) was lower than HD and MAE significantly. Eucalyptol, copaene, borneol, bornyl acetate, terpinene 4-acetate, caryophyllene, terpineol and p-methylhydrocinnamic aldehyde were other major compositions of MAE that detected in higher percent content than HD and SFE. Eucalyptol was only detected in HD (1.19%) and MAE (3.12%), meanwhile SFE was not detected. The major compositions in terpene class such as borneol, bornyl acetate, terpinene 4-acetate, caryophyllene and terpineol were detected in MAE at higher rate than HD and SFE. However, SFE was detected at least 7 major compositions that not detected in HD and MAE. Especially, heptadecane (10.70%) and pentadecane (3.55%) were only founded in essential oil from SFE at very high rate. In case of the organic acid results, trans-o-coumaric acid from SFE was 9.86 % that higher than HD (0.98%) and MAE (1.58%), meanwhile hydrocinnamic acid, α-Linoleic acid, n-hexadecanoic acid were only detected by SFE.

The total of volatile aldehyde contents of HD, MAE and SFE in this study were 72.49%, 58.96% and 38.09% respectively. The results of total aldehyde compositions shown relative contents lower

than the previous report [9] that used stream-distillation (SD), ultrasonic-assisted stream distillation (UASD) and microwave assisted stream distillation (MASD). However, the total compositions of terpene class that obtained in this study were higher than significantly. The results of HD, MAE and SFE presented compositions in terpene class at 19, 20 and 21 contents respectively. MAE presented the most major compositions in terpene class at 8 compositions, meanwhile HD and SFE were 4 and 2 compositions. In comparison of total relative contents for terpene class, MAE presented the highest rate at 26.77%, meanwhile HD and SFE were 12.98% and 10.42%. Cinnamyl acetate which is chemical composition of the cinnamyl ester family was also detected from HD, MAE and SFE. Cinnamyl acetate is also known as the volatile substance that affected to taste and fragrance of cinnamon [19]. The results of cinnamyl acetate that obtained from HD and MAE in this study were slightly higher than the previous study [9]. Although, cinnamyl acetate relative content of SFE was detected at lower rate than HD and MAE but It remain presented higher rate more than the result from cinnamon oil obtained by SFE in previous study [11]. Although, HD and MAE were shown better results on volatile aldehyde, terpene and some of the ester compositions. In the other hand, SFE was presented strongly results on alkane hydrocarbon, phenolic acid and alcohol. Heptadecane and pentadecane which are alkane was obviously chemical compositions that detected only in SFE. Furthermore, phenolic acid such as coumaric acid and cinnamic acid were detected from SFE result at high content. Both coumaric acid and cinnamic acid were also found in essential oils from cinnamon bark that extracted by different methods in previous reports [3,24,25].

Table 4. The compositions of cinnamon essential oils from HD, MAE and SFE

No	Chemical composition	Relative content/%			Molecular formula
		HD	MAE	SFE	
1	α-Pinene	0.21	0.90	0.03	$C_{10}H_{16}$
3	β-Pinene	0.51	0.48	0.08	$C_{10}H_{16}$
4	D-Limonene	0.86	0.57	0.06	$C_{10}H_{16}$
5	Eucalyptol	**1.19**	**3.02**	-	$C_{10}H_{18}O$
6	γ-Terpinene	0.04	0.16	-	$C_{10}H_{16}$
7	o-Cymene	0.10	0.11	-	$C_{10}H_{14}$
8	α-Cubebene	0.04	0.24	0.04	$C_{10}H_{24}$
9	Copaene	**1.73**	**3.01**	**1.69**	$C_{15}H_{24}$
10	Pentadecane	-	-	**3.55**	$C_{15}H_{32}$
11	Linalool	0.40	0.44	-	$C_{10}H_{18}O$
12	cis-.alpha.-Bergamotene	0.15	0.47	0.38	$C_{15}H_{24}$
13	Borneol	0.80	**4.09**	0.19	$C_{10}H_{18}O$
14	Bornyl acetate	**1.37**	**2.94**	0.28	$C_{12}H_{20}O_2$
15	Terpinene 4-acetate	**1.41**	**2.47**	0.28	$C_{12}H_{20}O_2$
16	Caryophyllene	0.87	**2.39**	**4.01**	$C_{15}H_{24}$
17	2-Methylbenzofuran	0.21	0.13	-	C_9H_8O
18	1,4,7,-Cycloundecatriene, 1,5,9,9-tetramethyl-, Z,Z,Z-	-	0.34	0.56	$C_{15}H_{24}$
19	Estragole	-	-	0.30	$C_{10}H_{12}O$
20	(E)-.beta.-Famesene	-	-	0.16	$C_{15}H_{24}$
21	Terpineol	**1.86**	**3.14**	0.37	$C_{10}H_{18}O$

22	Cyclosativene	-	-	0.63	$C_{15}H_{24}$
23	Heptadecane	-	-	**10.70**	$C_{17}H_{36}$
24	Lemnalol	0.15	0.66	0.10	$C_{15}H_{24}O$
25	(Z)-2- Methoxycinnamaldehyde	0.33	**5.88**	**1.31**	$C_{10}H_{12}O$
26	Dysoxylonene	0.92	0.38	0.58	$C_{15}H_{24}$
27	2,4-Decadienal	0.11	0.13	-	$C_{10}H_{16}O$

Table 4. Continueted

28	cis-Calamenene	0.15	0.23	0.14	$C_{15}H_{22}$
29	n-Heneicosane	-	-	0.51	$C_{11}H_{44}$
30	Z-5-Nonadecene	-	-	**1.20**	$C_{19}H_{38}$
31	Cinnamaldehyde	**72.16**	**53.08**	**36.78**	C_9H_8O
32	Humulene epoxide 2	-	0.03	0.44	$C_{15}H_{24}O$
33	Epicubenol	0.25	0.40	0.50	$C_{15}H_{26}O$
34	Cinnamyl acetate	**10.52**	**9.76**	**3.45**	$C_{11}H_{12}O_2$
35	o-Eugenol	0.20	0.94	**2.96**	$C_{11}H_{12}O_2$
36	α-Cadinol	0.11	0.78	0.20	$C_{15}H_{26}O$
37	Piperonal	-	-	0.31	$C_8H_6O_3$
38	Isoeugenol acetate	-	0.33	**1.15**	$C_{12}H_{14}O_3$
39	Styryl carbinol	0.22	0.39	**1.66**	$C_9H_{10}O$
40	Palmitoleic acid	-	-	0.20	$C_{16}H_{30}O_2$
41	Coumaric acid	0.98	**1.58**	**9.86**	$C_9H_8O_3$
42	α-Linoleic acid			0.36	$C_{18}H_{30}O_2$
43	Ethyl p-methoxycinnamate	-	0.03	**1.13**	$C_{12}H_{14}O_3$
44	Xanthorrhizol	-	-	0.81	$C_{15}H_{22}O$
45	Cinnamic acid	-	-	**1.20**	$C_9H_{10}O_2$
46	Pellitorine	-	-	**1.55**	$C_{14}H_{25}NO$
47	Platambin	-	-	0.69	$C_{15}H_{26}O_2$
48	Eicosen-1-ol, cis-9-	-	-	0.37	$C_{20}H_{40}O$
49	Hexanedioic acid, bis(2-ethylhexyl) ester	-	-	0.76	$C_{22}H_{42}O_4$
50	Phenylpropanamide	-	-	0.71	$C_9H_{11}NO$
51	1-Cyclohexene-1-ethanol, 2,6,6-trimethyl-	-	-	**2.44**	$C_{11}H_{20}O$
52	n-Hexadecanoic acid	-	-	0.93	$C_{16}H_{32}O_2$
53	Squalene			0.22	$C_{30}H_{50}$
54	Tetracosane	-	-	0.29	$C_{24}H_{50}$
55	Cinnamoylpiperidine	-	-	0.38	$C_{14}H_{17}NO$
56	Methyl piperate	-	-	**2.37**	$C_{13}H_{12}O_4$
	Total	97.85	99.47	98.87	

CONCLUSION

The optimization of process parameters for MAE for the extraction of cinnamon (Cinnamomum verum J.Presl) was investigated in this study. The highest yield obtained from MAE under the analysis of RSM was found at microwave power (662 W), extraction time (36.8 min) and solid to liquid ratio (100g/513mL). Extraction oil yield of MAE (2.86%) was higher than HD (2.13%) but lower than SFE (6.83%). From the result of ANOVA, the process parameters that extremely effected on essential oil yield of MAE were extraction time, microwave power and solid/liquid ratio respectively. The values of determination coefficient (R^2) and the adjusted determination coefficient (R^2_{Adj}) were 0.990 and 0.974 respectively that indicated a high degree of positive correlation between predicted and actual values. MAE was also presented better results on compositions in terpene class than HD and SFE. However, HD was presented the most of cinnamaldehyde content, meanwhile SFE was presented better results on compositions in phenolic and alcohol class. Due to the different of heat generation mechanism between HD and MAE, the benefits of MAE were provided higher extraction yield in shorter time and detected more compositions than HD. Although, SFE presented more advantages in extraction yield and composition content than other. In the other hand, disadvantages of SFE were higher cost of extraction process and longer extraction time than MAE. Hence, MAE is recommended as reasonable process to extract essential oil from cinnamon.

REFERENCES

1. Jeyaratnam, N., Nour, A.H., Kanthasamy, R., Nour, A.H., Yuvaraj, A.R. and Akindoyo, J.O. (2016). Essential oil from Cinnamomum cassia bark through hydrodistillation and advanced microwave assisted hydrodistillation. Ind. Crop. Prod, 92, 57–66.
2. Nabavi, F.S., Lorenzo, A.D., Izadi, M., Sobarzo-Sánchez, E., Daglia, M. and Nabavi, M.S. (2015). Antibacterial effects of cinnamon: From farm to food, cosmetic and pharmaceutical industries. Nutrients, 7, 7729–7748.
3. Zaizhi, L., Hualan L., Guoqiang C., Mengxia W., Zhengrong Z. and Haiyan N. (2021). Efficient extraction of essential oil from Cinnamomum burmannii leaves using enzymolysis pretreatment and followed by microwave-assisted method. LWT, 147, 1-11.
4. MedThai, accessed 2 August 2017, <https://medthai.com/cinnamon/>
5. B. Ren, C. Chen, C. Li, X. Fu, L. You and R.H. Liu, (2017) Optimization of microwave-assisted extraction of Sargassum thunbergii polysaccharides and its antioxidant and hypoglycemic activities. Carbohydrate Polymers, 173, 192-201.
6. Enwei, W., Rui, Y., Hepeng, Z., Penghui, W., Suqing, Z., Wanchen, Z., Yang, Z. and Hongli, Z. (2019). Microwave-assisted extraction releases the antioxidant polysaccharides from seabuckthorn (Hippophae rhamnoides L.) berries. International Journal of Biological Macromolecules, 123, 280-290.
7. S. Rahmati, A. Abdullah and O.L. Kang. (2019) Effects of different microwave intensity on the extraction yield and physicochemical properties of pectin from dragon fruit (Hylocereus polyrhizus) peels. Bioactive Carbohydrates and Dietary Fibre, 18, 1-8.
8. Hyun-Gyu. L., Yunhee, J., Kashif, A. and Joong-Ho, K. (2018). Optimization of green extraction methods for cinnamic acid and cinnamaldehyde from Cinnamon (Cinnamomum cassia) by response surface methodology. Food Sci Biotechnol, 27(6), 1607-1617.
9. Yu, T., Yao, H., Qi, S. and Wang, J. (2020). GC-MS analysis of volatiles in cinnamon essential oil extracted by different methods. GRASAS Y ACEITES, 71(3), 1-8.

10. Saeedeh, G. and Ghasem, N. (2022). Evaluation of the extraction process parameters on bioactive compounds of cinnamon bark: A comparative study. Process Biochemistry, 114, 93-101.
11. Hadi, B., Mohammad, N. L., and Ali, H. A., (2011). Effects of some experimental parameters on yield and composition of supercritical carbon dioxide extracts of cinnamon bark. Journal of Food Process Engineering, 34, 293-303.
12. Lijun, S., Pengzhan, L., Yinzhuo, Y., Ying, H., Bingyao, B., Xujie, H. and Li, Z. (2019). Supercritical CO2 fluid extraction of flavonoid compounds from Xinjiang jujube (Ziziphus jujuba Mill.) leaves and associated biological activities and flavonoid compositions. Industrial Crops & Products, 139, 1-8.
13. Serhat, B., Münevver, S., Ezgi, A. and Atalay, S. (2019). Conventional and supercritical fluid extraction (SFE) of colchicine from Colchicum speciosum. Industrial Crops & Products, 128, 80-84.
14. Y. Wang, Z.T. Jiang, R. Li and W.Q. Guan, (2013). Composition Comparison of Essential Oils Extracted by Microwave assisted Hydrodistillation and Hydrodistillation from Kaempferia galanga L. Grown in China. Journal of Essential Oil Bearing Plants, 12:4, 415-421.
15. G.A. Cardoso-Ugarte, G.P. Juarez-Becerra, M.E. Sosa-Morales and A. Lopez-Malo, (2013). Microwave-assisted Extraction of Essential Oils from Herbs. Journal of Microwave Power and Electromagnetic Energy, 47(1), 63-72.
16. Juan, G., Rifu, Y., Yu Shi, G., Kun, H., Yong, H. and FengLin, S. (2021). Optimization and evaluation of the ultrasound-enhanced subcritical water extraction of cinnamon bark oil. LWT, 147, 1-10.
17. Gopu, C. L., Aher, S., Mehta, H., Paradkar, A. R. and Mahadik, K. R. (2008). Simultaneous determination of cinnamaldehyde, eugenol and piperine by HPTLC densitometric method. Phtochemical Analysis, 19, 116-121.
18. Imen, K., Bilel, H., Bochra, G., Amina, C., Saloua, L., Radhouane, G., Ahmed, B., and Ezeddine, B. M. (2019). Optimization of Cinnamon (Cinnamomum zeylanicum Blume) Essential Oil Extraction: Evaluation of Antioxidant and Antiproliferative Effects. Evidence-Based Complementary and Alternative Medicine, volume 2019, 1-11.
19. Mohammad, H. E., Fereshteh, G., Zeinolabedin, B. S., Hossein, S. A., and Mehdi, M. (2013). Optimization of Superheated Water Extraction of Essential Oils from Cinnamon Bark Using Response Surface Methodology. TEOP, 16(6), 740-748.
20. Ameer, K., Bae, S.W., Jo, Y., Chung, N., Gao, Y. and Kwon J. H. (2017). Optimization and modeling for heat reflux extraction of total yield, stevioside and rebaudioside-A from Stevia rebaudiana (Bertoni) leaves. Sep. Sci. Technol. 52, 1193–1205.
21. Maran, J.P., and Prakash, K. A. (2015). Process variables influence on microwave assisted extraction of pectin from waste Carcia papaya L. peel. International Journal of Biological Macromolecules, 73, 202-206.
22. Eva, D., Marie, S., Lucie, C. and Petr Hrdlicka. (2015). Effects of Extraction Methods on the Phenolic Compounds Contents and Antioxidant Capacities of Cinnamon Extracts. Food Sci. Biotechnol, 24(4), 1201-1207.
23. Nitthiyah, J., Abdurahman, H. N. and John, O. A. (2016). The potential of microwave assisted hydrodistillation in extraction of essential oil from Cinnamomum Cassia (cinnamon). ARPN Journal of Engineering and Applied Sciences, 11(4), 2179-2183.

24. Li, Y.-q., Kong, D.-x., & Wu, H. (2013). Analysis and evaluation of essential oil components of cinnamon barks using GC–MS and FTIR spectroscopy. Industrial Crops and Products, 41, 269-278.