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Extraction and Potential of Cinnamon Essential Oil towards Repellency and Insecticidal Activity

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Abstract- The potential of Cinnamon essential oil as a natural insecticides and ants repellent was studied. *Cinnamon cassia* bark was extracted using hydrodistillation and soxhlet extraction method with three different solvents i. e. petroleum ether, hexane and dichloromethane. All extraction was carried out for 6 hours at 1 atm. The highest yield of cinnamon oil was obtained by soxhlet extraction in dichloromethane, followed by hexane and petroleum ether were 5.22 %, 3.84 % and 3.71 %, respectively. While only 1.82 % yields of cinnamon essential oil extracted when using hydrodistillation method. The volatile compounds of cinnamon essential oil were identified using GC-MS analysis. The results indicated that 9 major volatile compound were presence such as alcohols, aldehydes, alkenes, carboxylic acids, ether, ester and ketone in the cinnamon essential oil extracted by hydrodistillation. Trans-cinnamaldehyde was found to be the major volatile compound with the highest percentage of 86.67 % by soxhlet extraction using hexane. The repellency and insecticidal activity of cinnamon oil by hydrodistillation method obtained was directly exposed to specimen i.e., ants. The repellency and insecticidal activity of cinnamon essential oil was compared through different concentration of fabricated repellency paper. As a conclusion, solvent extraction shows an effective method on cinnamon essential oil extraction with positive insecticidal and repellent activity on ants.

Index Terms- Cinnamon essential oil, GC-MS, trans-cinnamaldehyde, repellent, insecticidal activity, soxhlet extraction, hydrodistillation

I. INTRODUCTION

Essential oils are volatile natural complex secondary metabolites which has a strong odor and have a generally lower density than water (Bruneton, 1999; Bakkali et al., 2008). Approximately, 3,000 esential oils are known out of which 300 that have been commercialized for cosmetics, pharmaceuticals, perfume industries (Bakkali et al., 2008) and pesticidal potential (Franzios et al., 1997; Chang and Cheng, 2002).

Cinnamon is a spice collected from the bark of several trees from the genus Cinnamomum and Lauracea family that is used in sweet and savoury foods. According to Vangalapati et. al (2012), *Cinnamon Cassia (C. Cassia)* has the strong and spicy-sweet flavour. *Vietnamese cassia* (*Saigon cinnamon*, *Cinnamomum loureiroii*) and *Chinese cassia* (*Cinnamomum aromaticum*) are the sweetest and strongest varieties. As stated by Janick and Jules, (2011), the name cinnamon comes through the Greek kinnámōmon from Phoenician. In Sinhala, Sri Lanka, cinnamon is known as kurundu which was recorded in English in the 17th century as Korunda (Knox and Robert, 2008). In Indonesia, where cinnamon is cultivated in Java and Sumatra, it is called kayu manis ("sweet wood") and sometimes *cassia vera*, the "real" *cassia* (Samat and Bell, 2009).

Repellent is defined by Fried et al. (2007) as substances that cause insect to turn away. Repellent have been used to prevent insects or specifically in this study, the ants from harming or annoying human daily life as they always swarm over host's food especially food that have been left on tables or being uncovered. Ant repellent is used to prevent the ants from invading the houses and spoiling the foods. Chemicals and poisonous substances are effective, but can bring harmful in the kitchen, around children and pets. One of the example of carcinogenic chemical that have been used which either repell or kill the ants is N,N-diethyl-3-methylbenzamide (DEET). Therefore, an alternative natural repellent from cinnamon oil have been developed to replace the carcinorgenic chemical repellent.

In this study, the extraction of the cinnamon essential oil was carried out by hydrodistillation in a Clavenger-type apparatus in accordance with the method of Wang et al. (2009) with slight modification and using Soxhlet extraction in accordance with the method of Mustafa and Hilal (2004) using three different solvents which are dichloromethane (DCM), hexane and petroleum ether. The cinnamon essential oil was analyzed using gas chromatography–mass spectrometry (GC-MS) to determine the chemical compound especially the cinnamaldehyde. The cinnamon essential oil was also used in this study to test for the repellency and insecticidal activity of the ants.

II. METHOD

Material and Chemicals

The Bark of *Cinnamon cassia sp* used in this study was purchased from a local supermarket. All solvents and chemical used such as hexane, dichloromethane, petroleum ether and anhydrous sodium sulphate were analytical grade.

Sample Preparation

Fresh bark sample was washed and air-dried, and then the dried sample was ground into powder . Then, the sample was stored in a drying oven for further analyses. In order to compare the extraction yield of cinnamon esential oil obtained, different extraction methods were used. Extraction of cinnamon oil was carried out using hydrodistillation and Soxhlet extraction with hexane, dicholoromethane and petroleum ether as the solvents.

Extraction of cinnamon oil using Hydrodistillation

The cinnamon essential oil was extracted by using hydrodistilation with a Clevenger type apparatus (Wang et al., 2009) with slight modification. About 30 gm of precisely weighed of cinnamon bark powder has been put into 500 mL distillation flask with four boiling chip and 300 mL of distilled water was poured into the flask. They were immersed for 1 hr, followed by heating at 100 ºC for 6 hrs. Then, the distillate was transferred to a 250 mL conical flask. Then, the volatile compounds was extracted from the water phase three times using dichloromethane and dehydrated over anhydrous sodium sulphate for 30 min and filtered through a mid-speed filter paper. The cinnamon oil obtained was concentrated and stored at 4 ºC for further analyses. The percentage yield of cinnamon essential oil has been calculated using the following formula.

$$\text{Percentage of essential oil} = \frac{\text{Essential oil weight}}{\text{sample weight}} \text{x100} \quad (1)$$

Extraction of Cinnamon Essential Oil using Soxhlet Extraction

The extraction of cinnamon essential oil was carried out using Soxhlet extraction method. An approximately 30 gm of cinnamon powder was placed into the extraction thimble and covered with glass wool to prevent floating. The round bottom flask containing boiling chips was weighed. Then 250 mL of hexane was poured into the round bottom flask. The soxhlet was heated at 65 ºC at 1 atm for 6 hrs (Mustafa and Hilal, 2004). The same method was applied to the other two solvents which are dichloromethane and petroleum ether. The heating temperature was changed to 60 ºC for petroleum ether and 40 ºC for dichloromethane. The percentage yield of oil was calculated using equation 1.

GC-MS Analysis

The determination of active component of volatile compound in essential oil of the plant performed on varians 4000 GC/MS/MS model. Column CP8944 30 m x 0.25 mm x 0.39 mm was used for separation. The oven temperature was raised from 40 °C to 230 °C at constant heating rate of 5 °C min^{-1}. The active compound in essential oil was identified using the attached software.

Preparation of Fabricated Repellency Paper

The paraffin wax was cut into smaller pieces and placed into the double boiler pan and set up to the high heat. After that, the essential oil of cinnamon was poured into the melted paraffin wax in the percentage concentration of 5 %. Then, a piece of packaging paper was dipped into the melting paraffin and cinnamon mixture. The paper was quickly lifted out of the wax and the paper was dried in less than a minute. The steps were repeated with different concentration of cinnamon essential oil which were 10 %, 15 %, and 20 % v/v. Fig. 1 showed the fabricated repellency paper for further analysis.

Figure 1: Fabricated Repellency Paper

Repellency Test

In the repellency test, the open exposure method has been applied. Ants were placed in the investigation area that contained different concentration of fabricated repellency paper and control paper (without cinnamon oil). The repellency of the ants will be recorded every 15 min for a total of 1 hr. After 1 hour, the percentage repellency was calculated by following formula according to Liu et al., (2006).

$$Repellency\ (\%) = \frac{(C - E)}{T}$$

C is the ant number in control paper, E is the ants number on fabricated repellency paper and T is the total insects in the investigating area. The calculated percentage of repellency was compared between different concentration of fabricated repellency paper and control paper.

Insecticidal test

The method of Appel *et. al* (2004) was slightly modified to determine the effectiveness of the cinnamon active paper in repelling or terminating the ants. In investigating the insecticidal activity of cinnamon, the close exposure method have been used. The fabricated repellency paper with their different concentrations of cinnamon essential oil was placed in the plastic containers and a control paper as a standard. Ants was transferred into covered container. The container was sealed by the wrapping plastic. Mortality was recorded every 15 min for a total of 90 min.

III. RESULTS AND DISCUSSION

Percentage Yield of Cinnamon Essential Oil via Hydrodistillation and Soxhlet Extraction

In this study, two methods of extraction were used to extract cinnamon essential oil for 6 hours extraction time using hydrodistillation and Soxhlet extraction method. Three different solvents were used in Soxhlet method which are petroleum ether (PE), hexane and dicholoromethane (DCM). Comprehensive comparison of the cinnamon essential oil obtained by these methods were revealed in Fig. 2.

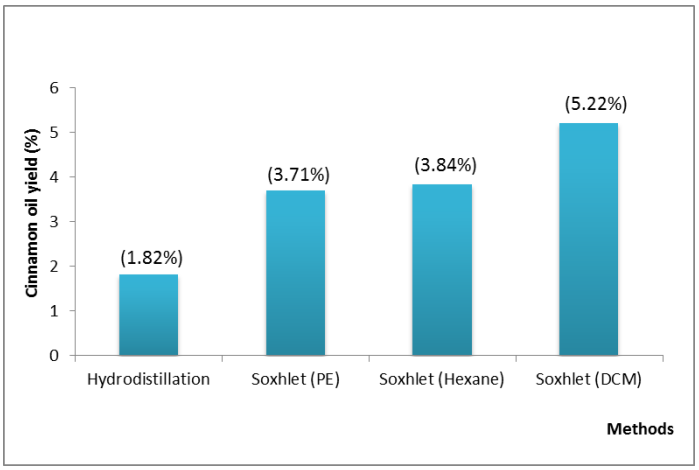

Figure 2 : Percentage yield of cinnamon essential oil via different extraction methods

Figure 4.1 indicates the essential oil yields of cinnamon bark using different extraction methods. The extraction by using soxhlet with different solvents, i.e. petroleum ether, hexane and dichloromethane was shown the significant differences between the percentage of yield obtained by the three solvents. The results showed that the highest percentage yield of cinnamon essential oil was by using dichloromethane followed by hexane and petroleum ether were 9.11 %, 3.84 % and, 3.71 %, respectively. These results were comparable with the previous study which showed that dichloromethane gave higher extracted yield due to hexane has highest selectivity (Slavco et al.,1998).

Extraction of cinnamon essential oil was also carried out by hydrodistillation method with conditions at ambient pressure of 1 atm, at temperature of 80 ºC and extraction time of 6 hrs. Cinnamon essential oil obtained via this method showed slightly higher about 1.82 % compared to Wang et al., (2009) which reported about 0.78-1.54 % only. Whereas Li et al., (2012) reported 1.3 % of oil yield when the cinnamon bark were extracted. From these results, the extraction method using the Soxhlet extraction gave higher percentage of cinnamon essential oil yield compared to hydrodistillation method.

GC-MS Analysis

The aim of this section is to qualitatively analyse volatile compounds in cinnamon essential oil using GC-MS. About 9 major volatile compounds, including alcohols, aldehydes, alkenes, carboxylic acid, ether, ester and ketone were detected in the cinnamon essential oil of *C.cassia* bark using hydrodistillation showed in Table 1. T*rans*-cinnamaldehyde was confirmed to be the major component with the highest area percentage of 84.97 %. The other main components included, 1,2-naphthalenedione, Ethanone and Borneol with area percentages of 9.03 %, 1.11 % and 1.03 %, respectively.

Furthermore, up to 13 volatile compounds were identified from *C.cassia* essential oil using Soxhlet method . *Trans*-cinnamaldehyde was the leading active volatile compound observed for 3 different solvent extraction used i.e., hexane, DCM and petroleum ether at 86.67 %, 68.47% and 79.43 %, respectively. Another main compounds were found in cinnamon oil i.e., 2H-1-benzopyran-2-one, 3-methyl-4-undecene, and 3-phenyl-2-propenal.

Table 1: Volatile compound identified from the cinnamon essential oil using different extraction method

Compounds	**Area (%) volatile compounds by different extraction method**			
		Soxhlet Extraction		
	Hydro-distillation	**Petroleum ether**	**Hexane**	**DCM**
Alcohol				
Borneol	1.03	-	-	-
3-cyclohexene-1 methanol	0.44	-	-	-
Bicyclohexane-2-ol	-	-	0.01	-
p-menth-1-en-8-ol	-	0.15	-	-
3-cyclohexen-1-ol	-	0.07	-	-
13-cyclohexene-1-methanol	-	-	-	0.07
Aldehyde				
Trans-cinnamaldehyde	84.97	68.47	86.67	79.43
Benzaldehyde	-	-	-	0.35
3-phenyl-2-propenal,	-	2.31	-	2.76
2-cyclopentene-1-butanal	-	-	0.05	-
Phenylglyoxal	-	-	0.04	-
Benzenepropanal	-	-	0.16	-
4-(2-methylcyclohex-1-enyl)-but-2-enal	-	-	-	-
Alkene				
Copaene	0.66	-	-	0.08
α-cubebene	-	0.31	0.67	-
Trans-α-Bergamotene	-	0.15	0.17	-
Caryophyllene	-	-	0.17	-
α-Calacorene	-	-	0.03	-
3-methyl-4-undecene	-	1.13	-	-
Alkane				
Dodecane,1-fluoro	-	0.06	-	-
Carboxylic acid				
Benzoic acid	0.24	-	-	-
Acetic acid	-	-	0.16	-
Propionic acid, thio-,S-isopentyl ester	-	0.26	-	-
Ester				
Phenbromate	0.18	-	-	-
Ether				
Methoxymethylbenzene	0.17	-	-	-
Benzenepropanoyl bromide	-	0.23	-	-
Eucalyptol	-	0.04	-	-
Ketone				
Ethanone	1.11	0.06	-	-
1,2-Napthalenedione	9.03	-	-	-
2H-1-Benzopyran-2-one	-	10.59	9.86	6.51

Cheng et al.,(2006) stated that cinnamaldehyde was the active compound in the cinnamon essential oil that has excellent inhibitory effect in controlling the red imported fire ant. The

percentage of the cinnamaldehyde obtained was compared with various method of extractions showed in Fig. 3.

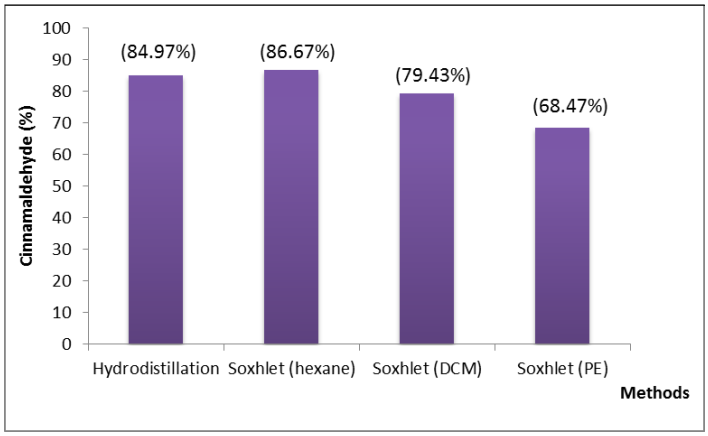

Figure 3 : Percentage of cinnamaldehyde from cinnamon essential oil via different extraction methods.

Based on Fig. 3, the cinnamaldehyde obtained by hydrodistillation was 84.97 % . It showed significant differences than the percentage of cinnamaldehyde reported by Li et al., (2012) which was 77.21 %. The results obtained from Soxhlet extraction method, the highest percentage of cinnamaldehyde was from the extraction using hexane which at 86.67 % followed by dichloromethane at 79.43 % and petroleum ether at 68.47 % of cinnamaldehyde. It is due to hexane was known to have the lowest polarity index compared to petroleum ether and dichloromethane. It is much more convenient to use hexane as it is highly non polar solvents and suitable to extract non polar substance such as oil. From these results, hydrodistillation method was almost as good as Soxhlet extraction using hexane method in obtaining high percentage of cinnamaldehyde.

In Fig. 4 spectrum chromatography of cinnamon essential oil and the retention time of cinnamaldehyde in the different extraction methods used in extraction of cinnamon essential oil. From the chromatogram, the retention time for all the cinnamaldehyde present in the cinnamon essential oil using various extraction methods were quite similar which at the average of 19.761 min at retention time.

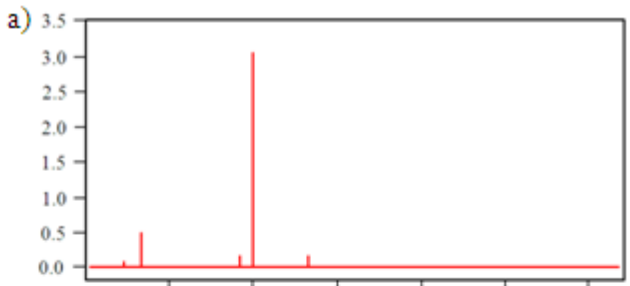

Figure 4: Spectrum chromatography and retention time of cinnamaldehyde in different type of extraction methods; (a) hydrodistillation, (b) hexane, (c) DCM, (d) petroleum ether.

Repellency and Insecticidal Activity

This repellency activity has been carried out to determine the repellency of ants toward fabricated repellency paper with the cinnamon essential oil applied on paper . While, insecticidal activity was carried out in a closed container for 90 min of exposure of 20 ants to the cinnamon essential oil and cinnamon powder paper. Mortality based on number of ants that died were recorded.

Repellency Test on Fabricated Repellency Paper

The repellency of ants toward paper coated with mixture of paraffin wax and cinnamon essential oil known as fabricated repellency paper were studied and shown in Fig. 5. The repellency activity was determined and compared by different concentration of cinnamon essential oil mixed in constant volume of paraffin wax.

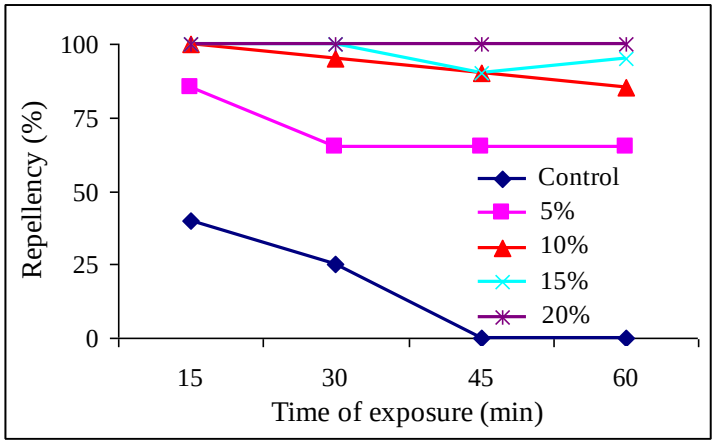

Figure 5: Repellency of ants on paper coated with mixture of cinnamon essential oil and paraffin wax

The results showed that the percentage of repellency increased with increasing concentration of cinnamon essential oil. At concentration of 20 % cinnamon essential oil, all ants completely repelled after 15 min and it continuosly gave 100 % of repellency after 60 min. When concentration decreased to 15 %, the repellency also decreased to 95 % after 60 min. Similar trend also observed for 10 % of cinnamon essential oil with a constant decrease in repellency from 100 % starting at 15 min to 85 % after total of 60 min. The concentration decreased to 5 % and the percentage of repellency also decreased to 65 % after 30 minutes and the percentage keep constant after 60 minutes. The repellency of control was 40 % at first 15 minutes and it declined until the repellency for control was 0 %. The results indicate that 20 % of cinnamon essential oil provide highest repellency performance.

Insecticidal Test on Fabricated Paper

The mortality of the ants were determined by different concentrations of fabricated repellency paper. Mortality of 20 ants were determined over 90 minutes of close exposure and the results were shown in Fig. 6.

An increased in concentration of cinnamon essential oil causes the mortality to increase. At concentration of 20 % cinnamon essential oil, it can terminated the ants completely after 90 min. This result was comparable to the study by Cheng et al.,(2006) that reported the cinnamaldehyde killed all the red ants after 90 minutes of exposure. Followed by 15 %, 10 % and 5 % of cinnamon essential oil gave the percentage mortality of 65 %, 50 % and 25 %, respectively after 90 min of close exposure.

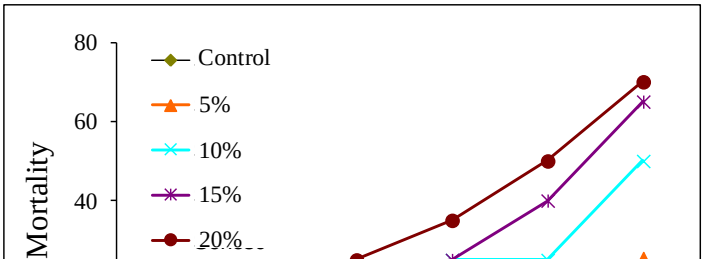

Figure 6: Mortality of ants by using cinnamon essential oil and paraffin wax mixture coated onto paper with different concentrations

III. CONCLUSION

Hydrodistillation and Soxhlet extraction with different solvents which are hexane, dichloromethane and petroleum ether were succesfully carried out to obtain the cinnamon essential oil yield from bark of *C.cassia.* Soxhlet extraction using dichloromethane as a solvent extraction shows the highest yield of cinnamon oil followed by hexane and petroleum were 5.22 %, 3.84 % and 3.71 %, respectively. While only 1.82 % yields of cinnamon essential oil extracted when using hydrodistillation method. GC-MS analysis indicated the apparent difference in the volatile compound compositions of cinnamon essential oil between various extraction methods. The total numbers of volatile compounds identified from hydrodistillation method, Soxhlet extraction using hexane, petroleum ether and dichloromethane were 9, 11, 13 and 6 respectively. Trans-cinnamaldehyde was found in the cinnamon essential oil extracted by each method, which was also the major volatile component that responsible for repellency and insecticidal activity of ants. Highest percentage of cinnamaldehyde obtained was from Soxhet extraction using hexane followed by hydrodistillation method, Soxhlet extraction using dichloromethane and the lowest using petroleum ether at 86.67 %, 68.47 % and 79.43 %, respectively. However, hydrodistillation method was almost as good as Soxhlet extraction using hexane method in obtaining high percentage of cinnamaldehyde.

In both repellency and insecticidal activity of ants, cinnamon essential oil shown a positive result which can repel and kill ants at certain concentrations. The highest concentration of cinnamon essential oil gave the highest mortality and repellency percentage and will be the effective and environmentally benign agents in ants control.

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