Characterization of Citrus Lemon (Peel Skin) Oil by using Soxhlet Extraction

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***Abstract*— The essential oil from Citrus Lemon peel has been extracted by using Soxhlet extraction method. 3 different organic solvents were chosen to perform the extraction which are Acetone, Chloroform and n-Hexane. The highest yield was found to be by using Chloroform as a solvent with 30.6627%, followed by Acetone (30.0613%) and n-Hexane (27.4790%). The Gas Chromatography Mass Spectrometry (GCMS) analysis and Fourier Transform Infrared Spectroscopy (FTIR) analysis has been conducted for the determination of component exist and functional group respectively. The analyses were conducted with the extraction time varied to 6 hours, first 3 hours and second 3 hours Firstly, for the extraction of oil by using Chloroform as a solvent, there are three main components were found to be dominant which are Coumarin, α-Pinene and 7H-Furo(3,2-g) (1) benzopyran-7-one,9-hydroxy- or commonly known as Psoralens (Furanocoumarins). As by using Acetone as a solvent in extraction, the dominant main compound was Benzoic acid, 2,4-dihydroxy-3, 5,6-trimethyl-, methyl ester. Meanwhile by using n-Hexane as a solvent, the dominant component was found to be n-Hexadecanoic acid or the common name for this component is palmitic acid. In addition, the FTIR spectra for Citrus Lemon fruit have been obtained where the principal vibration band was analyzed according to the available literature.**

Keywords*— *Lemon fruit, Soxhlet Extraction, GCMS (Gas Chromatography Mass Spectrometry), FTIR (Fourier Transfer Infrared Spectroscopy.

I. INTRODUCTION

Citrus species is one of the most popular world fruit crops which contain active phytochemicals. The example for citrus plants such as lemon, mandarin, lime, orange, sour orange and grapefruit belonging to the family of Rutaceae. This species is very well known as the species to supply many beneficial nutrients that may bring benefits to human being. The beneficial components that believed to be contains and provides by this species are folic acid, potassium, pectin and vitamin C. In addition, this species also proven to contribute to the prevention of life threatening diseases (Rafiq et al., 2018).

According to (Chaturvedi & Shrivastava Suhane, 2016) citrus lemon is the fruits that classified as citrus species and hybrid of the plant genus. Citrus lemon main characteristic is thorny branches, having white flowers, with edges that purple in colour, acidic, oval shaped juicy fruit, aromatic rind with yellow colour when ripe and also on it blossom end will have prominent bulge. This type of fruit is considered as an important medicinal plant of the Rutaceae family where the origin was from tropical and subtropical Southeast Asia. In crude extracts of different parts such as the viz, root, stem, leaves and flower of the lemon are proved to against clinically significant in bacterial strains. As for the lemon peel which is one of the waste or by-products from citrus lemon, this part contained of crude fibres (15.18%), crude fat (4.98%) and protein (9.42%). Besides, the lemon peel also contains of ash up to 6.26% and 5% acid contains in lemon juice causing lemon to have a sour taste where the pH is in the range of 2 to 3.

(Makni, Jemai, Kriaa, Chtourou, & Fetoui, 2018) stated that the number of world production for lemon are about 4,200,000 metric tons and this fruit is third most important citrus species after orange and mandarin. In fact, citrus lemon one of the species which is very rich with many important natural compounds such as citric acid, ascorbic acid, flavonoids, minerals as well as essential oil. Citrus fruits species typically widely use in food industries such as to produce fresh juice. Due to the reason that this species very rich in many important natural compounds especially in bioactive molecules such as natural antioxidants, flavonoids as well as phenolic acid, the peel which is the main friction of it waste that approximately has represent half of mass of the fruit, citrus lemon have been widely studied and there are many researches has been conducted regarding this fruit.

The study for the medicinal plants usually will starts with the pre-extraction and after that the procedures for the extraction, where it is an important step for processing of bioactive constituents that consists in plant materials. Soxhlet extraction or also known as solvent extraction is one of the method that typically used. This method is the simplest and easiest method. In addition, the process of extraction by using this method can be enhance by alteration in temperature as well as choosing of the suitable solvent (Azwanida, 2015).

According to (Rassem et al., 2016) the function of solvent extraction method is to separate a compound depend on the solubility of its parts. The process of extraction is done by using two separate liquids where the most common is by using water and an organic solvent. This method usually being chosen due to the factor can produce the higher amounts of essential oils and at the same time with lower cost. This type of extraction method also has been proven as the relatively simple as well as quite efficient. Solvent extraction method commonly being conducted by using the apparatus which known as Soxhlet extractor where it was designed to extract a lipid that consists in a solid material. This method allows the operation which is unmonitored and unmanageable while a small amount of solvent can be recycle efficiently. This apparatus is the conventional device where the solid-liquid contact are involves for the removal of one or also could be several types of compounds from solid materials and done by dissolution into a refluxing liquid phase. There are several advantages can be obtain by using this device such as the sample will be repeatedly brought into contact with the portions of solvent which is fresh, the procedure that being applied help to minimize the possibility for the solvent to become saturated with extractable material as well as the process to remove analyte from the matrix also can be enhance. In addition, the system temperature is close to the solvent boiling point and the heat which is excess energy will increase the system extraction kinetics.

As eloquently stated by (Khan & Dwivedi, 2018) the extraction process of solid material is the main reason for the designation of Soxhlet extractor. This equipment usually being used when the compounds are considered has a limited solubility for a solvent as well as when the impurities is insoluble in that solvent. By using this extractor, there are two phases will involve which are solid-liquid contact in order to removes one or more compounds from a solid by dissolving it into a refluxing liquid phase. The cavity which is being filled gradually with the extracting liquid phase by vapor condensation from distillation flask, is where the solid matrix is placed. As the liquid reaches the level that being preset, the contents in the cavity will be pulls by siphon back into the distillation flask which carrying the analytes that has been extracted into the bulk of liquid. In addition, the system temperature is closed to solvent boiling points. Hence, the heat which is the excess energy will cause the extraction kinetics in the system to be increase.

In addition, for the solvent extraction method the organic solvents such as ethanol, methanol, acetone, ethylene glycol or could be the mixture of solvents are applied and followed by centrifuging, filtering as well as vacuum concentration is suggested in order to obtain high efficiency of betacyanins. The different mixture of solvents also might help to increase the efficiency of the extraction process. As for ethanol which have the lower level of toxicity, it was the most favoured in the process of extraction for bioactive compounds (Fathordoobady, et al., 2016)

II. METHODOLOGY

A. Raw Materials

10 kg of Citrus Lemon fruits was purchased from Pasar Tani Seksyen 13, Shah Alam, Selangor. The sample of lemon fruits were washed, rinsed and dried using clean cloth. The lemon rind was removed carefully and chopped into smaller pieces by using slicer. The smaller pieces of lemon pieces were dried in a universal oven at Food Laboratory for 1 hour and 40 minutes at temperature of 75 ℃. The peel sample that has been dried were grinded to size of 0.5 µm by using grinder at Geology Laboratory in order to increase the efficiency of the results (Kusrini, et al, 2018).

B. Solvent Extraction

The process of extraction was performed by using Soxhlet extractor at Fluid Mechanics Laboratory. There are three different type of solvents has been used in this experiment which are Acetone, Chloroform and n-Hexane. 10 g of peels sample was used for each run. As for solvent, 200 mL was used per run. The experiment by using each solvent was run for 6 hours, first 3 hours and second 3 hours at temperature maintained as 150 ℃. The extracts were stored overnight, filtered and the solvent used was evaporated on vacuum rotary evaporator. The highest oil yield in between three different solvents was determined.

C. Gas Chromatography Mass Spectrometry (GCMS) Analysis

This analysis was conducted by using Gas Chromatography Mass Spectrometry (GCMS) equipment at Instrumentation Laboratory 1. The relative percentage for the constituents of oil was expressed as percentage by peak area normalization. The process to identify the components of essential oil was based on their retention indices (Yang & Kang, 2013).

D. Fourier Transform Infrared Spectroscopy (FTIR) Analysis

This analysis was conducted at the room temperature by using FTIR spectroscopy at Multipurpose Laboratory. Technique of pellet (pressed-disk) was performed. The spectral range was set in between (4000-400) cm^{-1}(Kamsonlian et al, 2011)

III. RESULTS AND DISCUSSION

A. Determination of Highest Percentage of Oil Yield

The study was started with solvent extraction method which performed by using Soxhlet extractor to complete the first objective. In this method there were three (3) different solvents were used. The organic solvents which are Acetone, Chloroform and n-Hexane has been chosen to complete this method. The experiment with 6 hours extraction time by using Soxhlet extractor was conducted by using each solvent. In order to determine the amount of oil yield obtained from Soxhlet extraction part, rotary evaporator method was performed afterward. The solvent with the highest percentage was determined and the results obtained are shown in Table 4.1 below.

Table 4.1: Percentage of oil yield by using different types of organic solvent

Solvent	Soxhlet Extractor		Rotary Evaporator		Percentage of oil yield (%)
	Weight of beaker + miscella (g)	Weight of miscella (g)	Weight of bottle + oil (g)	Weight of oil sample (g)	
Acetone	155.7559	58.5234	12.6688	3.8084	30.0613
Chloroform	178.5428	81.3103	12.7787	3.9183	30.6627
n-Hexane	133.9719	36.7394	12.2177	3.3573	27.4790

As shown in the results above, the highest percentage for yield of oil from citrus lemon peel was found to be by using Chloroform with the percentage of 30.6627 %. The results were followed by using Acetone and n-Hexane as a solvent with percentage of 30.0613 % and 27.4790 % respectively.

B. Soxhlet Extraction at Different Extraction Time

After the highest percentage of oil yield has been determined. The experiment was proceeded by performed Soxhlet extractor and rotary evaporator part by using the same solvent from part 1 which are Acetone, Chloroform and n-Hexane. In this part, the extraction time has been varied to 6 hours, first 3 hours and second 3 hours. The extraction time has been varied to performed GCMS and FTIR analysis to achieve the second objective which are to determine the component exist as well as functional group of oil from citrus lemon peel respectively.

C. GCMS Analysis

i) GCMS Analysis by using Chloroform as a Solvent

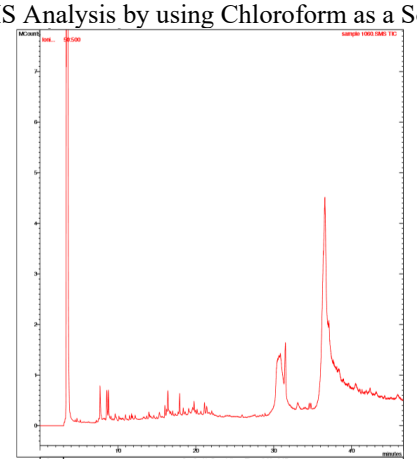

Figure 4.1: GCMS chromatogram of oil from Citrus Lemon peel for 6 hours extraction

Table 4.2: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database for 6 hours extraction

Peak Number	Retention Time (min)	Compound Name	% Amount
1	7.690	α-Pinene	0.1810
2	8.547	Thujone, trans / Bicyclo (3.1.0) hexane, 4-methyl-1-(1-methylethyl)-	0.1280
3	31.484	Acetamide, N-tert-butyl-2-(3-cyano-4,6-dimethylpyridin-2-ylsulfanyl)-	0.0345
4	32.766	Coumarin / 2H-1-Benzopyran-2-one,5,7-dimethoxy-	0.1970
5	34.542	7H-Furo(3,2-g) (1) benzopyran-7-one,9-hydroxy-	0.0293

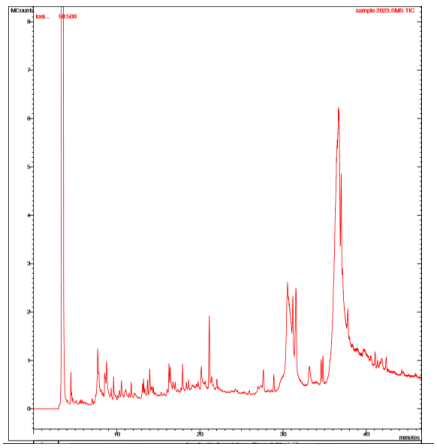

Figure 4.2: GCMS chromatogram of oil from Citrus Lemon peel for first 3 hours extraction

Table 4.3: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	16.412	Silane, (1-(5-ethenyltetrahydro-5-methyl-2-furanyl)-1-methylethoxy) trimethyl-, cis-	0.0251
2	31.159	Ethyl tridecanoate	0.1490
3	31.541	Coumarin / 2H-1-Benzopyran-2-one, 5,7-dimethoxy-	0.1670
4	33.157	7H-Furo (3,2-g) (1) benzopyran-7-one, 9-hydroxy-	0.0660
5	34.557	Imidazole, 2-amino-5-((2-carboxy) vinyl)-	0.0252

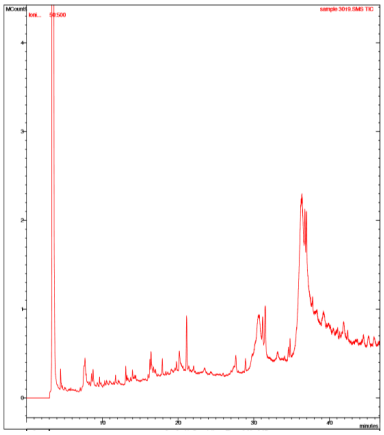

Figure 4.3: GCMS chromatogram of oil from Citrus Lemon peel for second 3 hours of extraction

Table 4.4: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	7.690	α-Pinene	0.0539
2	8.553	Bicyclo (3.1.1) hept-2-ene, 2,6,6-trimethyl-, (ṅ)-	0.0308
3	13.073	2H-Pyran-2-one, tetrahydro-4-hydroxy-4-methyl-	0.0452
4	31.498	Coumarin / 2H-1-Benzopyran-2-one, 5,7-dimethoxy	0.1010
5	36.349	D-streptamine, 0-2-amino-2-deoxy- α-D-glucopyranosyl-(13)- α-D-ribofuranosyl-(15)-2-deoxy-	0.0197

The components or compounds exist in the oil of Citrus Lemon peel by using Chloroform as a solvent are as shown in Table 4.2, Table 4.3 and Table 4.4 where each table represents the results for extraction time of 6 hours, first 3 hours and second 3 hours respectively. 5 major components were identified for three different extraction time that has been varied. At 6 hours of extraction, the main components exist were found to be Coumarin (0.1970%), α-Pinene (0.1810%) and Thujone, trans (0.1280%), Acetamide, N-tert-butyl-2-(3-cyano-4,6-dimethylpyridin-2-ylsulfanyl)- (0.0345%) and 7H-Furo(3,2-g) (1) benzopyran-7-one,9-hydroxy- (0.0293%). As for the first 3 hours of extraction, the main components were Coumarin (0.167%), Ethyl tridecanoate (0.1490%),7H-Furo (3,2-g) (1) benzopyran-7-one, 9-hydroxy- (0.0660%), Imidazole, 2-amino-5-((2-carboxy) vinyl)- (0.0252%) and Silane, (1-(5-ethenyltetrahydro-5-methyl-2-furanyl)-1-methylethoxy) trimethyl-, cis- (0.0252%). Meanwhile, for second 3 hours of extraction the main compounds exist were found to be Coumarin with the amount of (0.1010%), α-Pinene (0.0539%), 2H-Pyran-2-one, tetrahydro-4-hydroxy-4-methyl- (0.0452%), Bicyclo (3.1.1) hept-2-ene, 2,6,6-trimethyl-, (ṅ)- (0.0308%) and D-streptamine, 0-2-amino-2-deoxy- α-D-glucopyranosyl-(13)-α-D-ribofuranosyl-(15)-2-deoxy- (0.0197%).

ii) GCMS Analysis by using Acetone as a Solvent

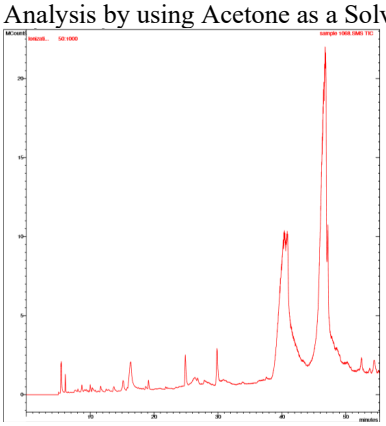

Figure 4.4: GCMS chromatogram of oil from Citrus Lemon peel for 6 hours extraction

Table 4.5: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database for 6 hours extraction

Peak Number	Retention Time (min)	Compound Name	% Amount
1	6.089	O-Xylene	0.1100
2	24.880	Phenol, 2,4-bis (1,1-dimethylethyl)-	0.1460
3	29.848	Benzoic acid, 2,4-dihydroxy-3, 5,6-trimethyl-, methyl ester	0.3510
4	46.533	2H-Pyran, 2-(7-dodecynyloxy) tetrahydro-	0.1400
5	47.175	9,9-Dimethoxybicyclo (3.3.1) nona-2, 4-dione	0.4150

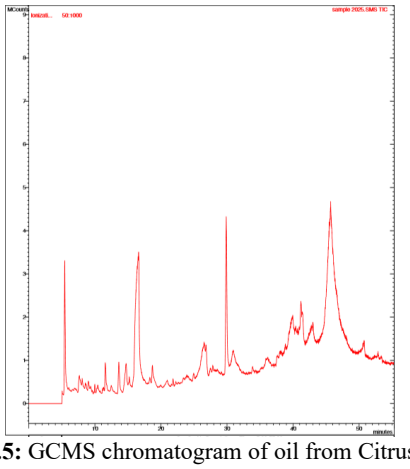

Figure 4.5: GCMS chromatogram of oil from Citrus Lemon peel for first 3 hours extraction

Table 4.6: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	11.570	3,6-Pyridazinedione,1,2-dihydro-4-methyl	0.0565
2	13.611	4H-Pyran-4-one, 2,3-dihydro-3, 5-dihydroxy-6-methyl-	0.2110
3	16.601	2-Furancarboxaldehyde, 5-(hydroxymethyl)-	0.3410
4	18.689	2-Methoxy-4-vinylphenol	0.1440
5	29.881	Benzoic acid,2,4-dihydroxy-3,5,6-trimethyl-, methyl ester	0.9401

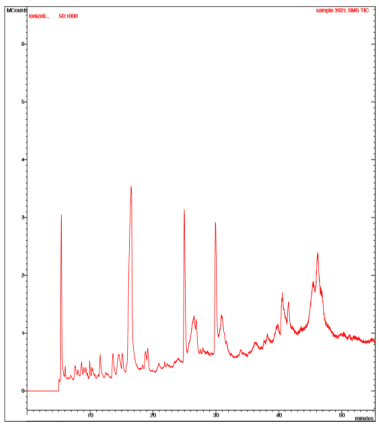

Figure 4.6: GCMS chromatogram of oil from Citrus Lemon peel for second 3 hours of extraction

Table 4.7: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	11.580	Furyl hydroxymethyl ketone	0.1320
2	16.547	1H-Pyrazole, 4,5-dihydro-3-methyl-1-propyl-	0.4220
3	19.150	Furane-2-carboxaldehyde, 5-(2,4,6-trichlorophenoxymethyl)-	0.1090
4	24.975	Phenol, 2-1(1,1-dimethylethyl)-4-(1,1,3,3-tetramethylbutyl)-	0.5340
5	29.943	11-Oxatetracyclo (5.3.2.0 (2,7).0 (2,8)) dodecan-9-one	1.0400

The components or compounds exist in the oil of Citrus Lemon peel by using Acetone as a solvent are as shown in Table 4.5, Table 4.6 and Table 4.7 where each table represents the results for extraction time of 6 hours, first 3 hours and second 3 hours respectively. 5 major components were identified for three different extraction time that has been varied. At 6 hours of extraction, the main components exist were found to be 9,9-Dimethoxybicyclo (3.3.1) nona-2, 4-dione (0.4150%), Benzoic acid, 2,4-dihydroxy-3, 5,6-trimethyl-, methyl ester (0.3510%), Phenol, 2,4-bis (1,1-dimethylethyl)- (0.1460%),2H-Pyran, 2-(7-dodecynyloxy) tetrahydro- (0.1400%) and O-Xylene (0.1100%). As for the first 3 hours of extraction, the main components were Benzoic acid,2,4-dihydroxy-3,5,6-trimethyl-, methyl ester (0.9401%), 2-Furancarboxaldehyde, 5-(hydroxymethyl)- (0.3410%), 4H-Pyran-4-one, 2,3-dihydro-3, 5-dihydroxy-6-methyl- (0.2110%), 2-Methoxy-4-vinylphenol (0.1440%) and 3,6-Pyridazinedione,1,2-dihydro-4-methyl (0.0565%). Meanwhile, for second 3 hours of extraction the main compounds exist were found to be 11-Oxatetracyclo (5.3.2.0 (2,7).0 (2,8)) dodecan-9-one with the amount of (1.0400%), Phenol, 2-1(1,1-dimethylethyl)-4-(1,1,3,3-tetramethylbutyl)- (0.5340%), 1H-Pyrazole, 4,5-dihydro-3-methyl-1-propyl- (0.4220%), Furyl hydroxymethyl ketone (0.1320%) and Furane-2-carboxaldehyde, 5-(2,4,6-trichlorophenoxymethyl)- (0.1090%).

iii) GCMS Analysis by using n-Hexane as a Solvent

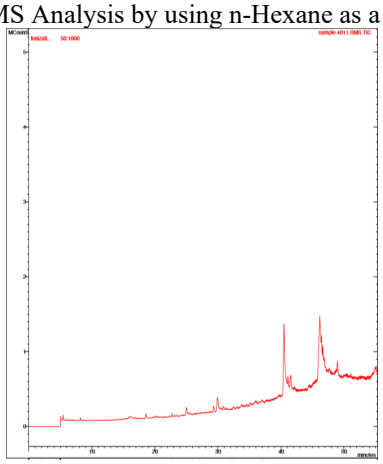

Figure 4.7: GCMS chromatogram of oil from Citrus Lemon peel for 6 hours extraction

Table 4.8: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database for 6 hours extraction

Peak Number	Retention Time (min)	Compound Name	% Amount
1	25.000	Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters	0.0609
2	29.920	Ethanone, 1,1'-(3-amino-2,4-pyridinediyl) bis-	0.0822
3	40.463	n-Hexadecanoic acid	0.4870
4	41.522	2H-1-Benzopyran-2-one, 5,7-dimethoxy-	0.1550
5	46.145	Glycyl-L-histidyl-L-lysine acetate	0.0851

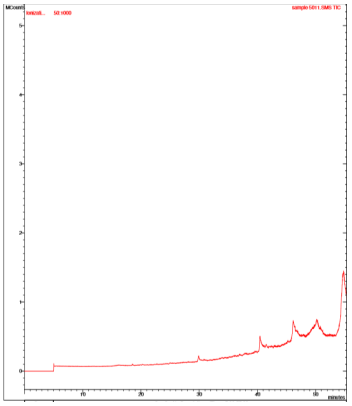

Figure 4.8: GCMS chromatogram of oil from Citrus Lemon peel for first 3 hours extraction

Table 4.9: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	29.896	Ethanone, 1,1'- (3-amino-2, 4-pyridinediyl) bis-	0.0430
2	40.430	Octane, 1-(ethenylthio)-	0.1660
3	46.152	Dodecane, 5,8-diethyl-	0.0346
4	50.198	9,9'-Biphenanthrene, octacosahydro-	0.0582
5	58.860	Cyano-(5-cyano-4,4,5-trimethyl-pyrrolidin-2-ylidene)-acetic acid	0.0800

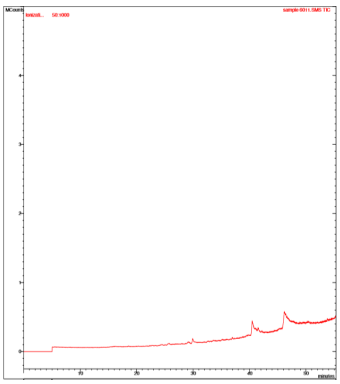

Figure 4.9: GCMS chromatogram of oil from Citrus Lemon peel for second 3 hours of extraction

Table 4.10: Identification of compound exist in oil of Citrus Lemon peel by using a retention time database

Peak Number	Retention Time (min)	Compound Name	% Amount
1	29.918	Phenol, 2-ethoxy-4-(2-propenyl)-	0.0280
2	40.461	n-Hexadecanoic acid	0.2120
3	41.508	2H-1-Benzopyran-2-one, 4,7-dimethoxy-	0.0552
4	42.167	2-Propene (dithioc) acid, 3-(4-ethoxyphenyl)-3-hydroxy-	0.0464
5	46.183	11-Oxa-dispiro (4.0.4.1) undecane-1-ol	0.2350

The components or compounds exist in the oil of Citrus Lemon peel by using n-Hexane as a solvent are as shown in Table 4.8, Table 4.9 and Table 4.10 where each table represents the results for extraction time of 6 hours, first 3 hours and second 3 hours respectively. 5 major components were identified for three different extraction time that has been varied. At 6 hours of extraction, the main components exist were found to be n-Hexadecanoic acid (0.4870%), 2H-1-Benzopyran-2-one, 5,7-dimethoxy- (0.1550%), Glycyl-L-histidyl-L-lysine acetate (0.0851%), Ethanone, 1,1'-(3-amino-2,4-pyridinediyl) bis- (0.0822%) and Pentanoic acid, 5-hydroxy-, 2,4-di-t-butylphenyl esters (0.0609%). As for the first 3 hours of extraction, the main components were Octane, 1-(ethenylthio)- (0.1660%), Cyano-(5-cyano-4,4,5-trimethyl-pyrrolidin-2-ylidene)-acetic acid (0.0800%), 9,9'-Biphenanthrene, octacosahydro- (0.0582%), Ethanone, 1,1'-(3-amino-2, 4-pyridinediyl) bis- (0.0430%) and Dodecane, 5,8-diethyl- (0.0346%). Meanwhile, for second 3 hours of extraction the main compounds exist were found to be 11-Oxa-dispiro (4.0.4.1) undecane-1-ol with the amount of (0.2350%), n-Hexadecanoic acid (0.2120%), 2H-1-Benzopyran-2-one, 4,7-dimethoxy- (0.0552%), 2-Propene (dithioc) acid, 3-(4-ethoxyphenyl)-3-hydroxy- (0.0464%) and Phenol, 2-ethoxy-4-(2-propenyl)- (0.0280%).

D. FTIR Analysis

i) FTIR Analysis by using Chloroform as a Solvent

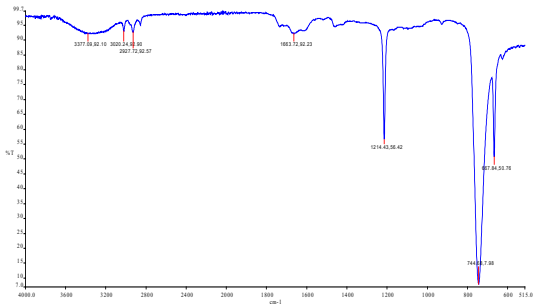

Figure 4.10: FTIR spectra for oil of Citrus Lemon at 6 hours of extraction time

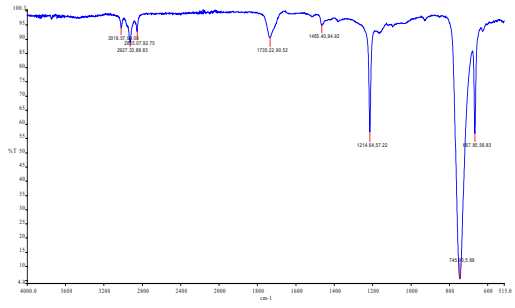

Figure 4.11: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

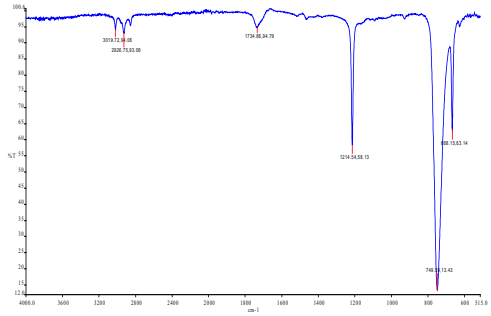

Figure 4.12: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

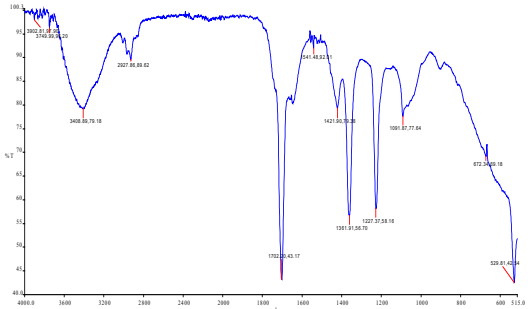

Figure 4.13: FTIR spectra for oil of Citrus Lemon at 6 hours of extraction time

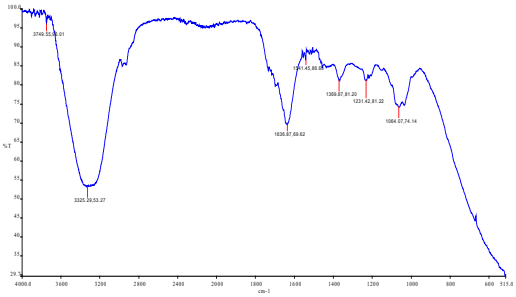

Figure 4.14: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

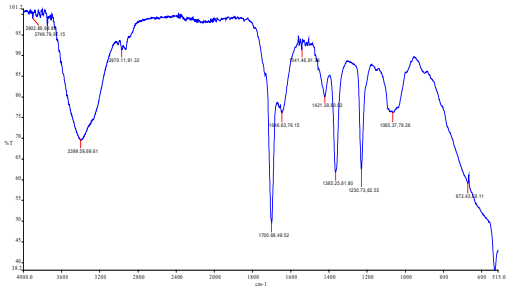

Figure 4.15: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

The vibration fundamentals from FTIR spectra for oil of Citrus Lemon peel by using Chloroform as a solvent are as presented in Figure 4.10, 4.11, 4.12 and functional groups has been identified based on the frequency peaks are listed in Table 4.14, 4.15 and 4.16 which represents the spectra results for 6 hours, first 3 hours and second 3 hours of extraction time respectively. The FTIR spectra were analyzed by comparing the results with the modes from the literature. The medium absorption peak of 3377.09 cm^{-1} for 6 hours of extraction displays the free and intermolecular bonded of hydroxyl groups were existed. The peaks of 3020.24 cm^{-1}, 3019.57 cm^{-1} and 3019. 72 cm^{-1} for the extraction of 6 hours, first 3 hours and second 3 hours respectively shows that the existence of aromatic – (C-H). The peak of 2927.72 cm^{-1} for 6 hours extraction time, first 3 hours extraction with 2927.33 cm^{-1} meanwhile second 3 hours extraction with 2926.75 cm^{-1}were due to CH stretching vibrations of CH, CH_2 and CH_3 groups. The peak at 2855.07 cm^{-1} presented in first 3 hours of extraction shows the existence of aldehyde – (C-H). As for the peaks which are 1735.22 cm^{-1} and 1734.86 cm^{-1} for the first 3 hours and second 3 hours of extraction is due to stretching vibrations of C=O. Meanwhile for the peak at 1663.72 cm^{-1} for 6 hours extraction was characteristics of C=C for aromatic rings. The peak of 1465.40 cm^{-1} for the first 3 hours of extraction is due to C-H bending. The peak at 1214.43 cm^{-1}, 1214.64 cm^{-1} and 1214.54 cm^{-1} presented for 6 hours, first 3 hours as well as second 3 hours of extraction respectively were due to the existence of C-O of aliphatic acid groups. In addition, for the additional peaks which are 744.68 cm^{-1} and 667.84 cm^{-1} for 6 hours of extraction, 745.90 cm^{-1} and 667.85 cm^{-1} for the first 3 hours of extraction as well as 749.59 cm^{-1} and 668.15 cm^{-1} for second 3 hours of extraction can be assigned to C=C bending modes for aromatic compounds.

ii) FTIR Analysis by using Acetone as a Solvent

The vibration fundamentals from FTIR spectra for oil of Citrus Lemon peel by using Acetone as a solvent are as presented in Figure 4.13, 4.14, 4.15 and functional groups has been identified based on the frequency peaks are listed in Table 4.17, 4.18 and 4.19 which represents the spectra results for 6 hours, first 3 hours and second 3 hours of extraction time respectively. The FTIR spectra were analyzed by comparing the results with the modes from the literature. During the 6 hours and second 3 hours of extraction with peaks of 3408.89 cm^{-1} and 3399.59 cm^{-1} respectively are due to N-H stretching which shows the possible involvement of hydroxyl groups. As for the first 3 hours with peak of 3325.29 cm^{-1} is due to O-H stretching. The peaks observed at 2927.86 cm^{-1} for 6 hours of extraction and 2970.11 cm^{-1} for second 3 hours of extraction can be appointed as stretching asymmetric vibration of CH group. As for the peaks of 1702.20 cm^{-1} and 1700.68 cm^{-1} for 6 hours and second 3 hours of extraction respectively are due to stretching vibrations of C=O. The strong peak of 1636.87 cm^{-1} for first 3 hours of extraction is due to C=C stretching. Meanwhile, for second 3 hours of extraction with medium peak of 1646.63 cm^{-1} is due to C=N stretching. During extraction time of 6 hours with strong peaks of 1541.48 cm^{-1} and 1361.91 cm^{-1}, first 3 hours with 1541.45 cm^{-1} and 1369.87 cm^{-1} and second 3 hours with 1541.46 cm^{-1} are due to N-O stretching. The peaks of 1421.90 cm^{-1} during 6 hours of extraction and second 3 hours of extraction with 1421.39 cm^{-1} and 1365.25 cm^{-1} were the characteristics of C=H bending. The C-O of aliphatic acid groups are attributed to the peaks of 1227.37 cm^{-1} and 1091.87 cm^{-1} for 6 hours of extraction, 1231.42 cm^{-1} and 1064.07 cm^{-1} for first 3 hours of extraction and 1230.73 cm^{-1} and 1065.37 cm^{-1} during second 3 hours of extraction. Furthermore, for the peaks of 672.34 cm^{-1} and 529.81 cm^{-1} at 6 hours of extraction as well as 672.43 cm^{-1} for

second 3 hours of extraction can be assigned to C=C bending modes of aromatic compounds

iii) FTIR Analysis by using n-Hexane as a Solvent

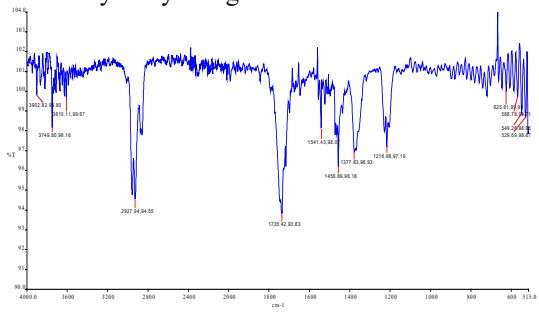

Figure 4.16: FTIR spectra for oil of Citrus Lemon at 6 hours of extraction time

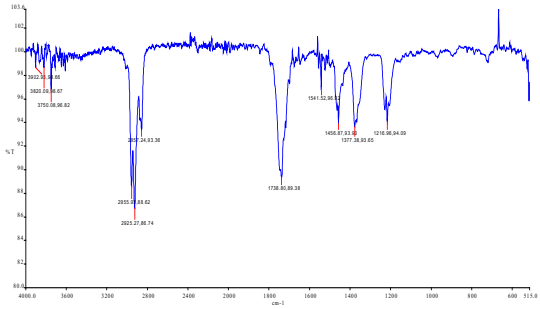

Figure 4.17: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

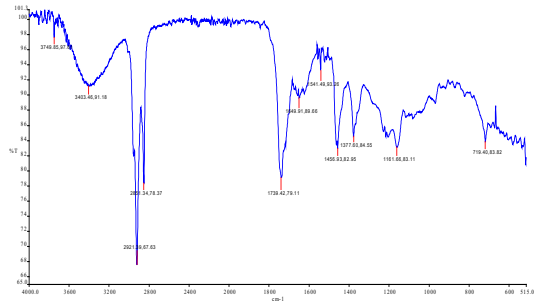

Figure 4.18: FTIR spectra for oil of Citrus Lemon at first 3 hours of extraction time

The vibration fundamentals from FTIR spectra for oil of Citrus Lemon peel by using n-Hexane as a solvent are as presented in Figure 4.16, 4.17, 4.18 and functional groups has been identified based on the frequency peaks are listed in Table 4.20, 4.21 and 4.22 which represents the spectra results for 6 hours, first 3 hours and second 3 hours of extraction time respectively. The FTIR spectra were analyzed by comparing the results with the modes from the literature. As shown in Figure 4.16 above, the peak of 3610.11 cm^{-1} for 6 hours of extraction is due to O-H stretching. The hydroxyl group is existed as shown from N-H stretching from peak of 3403.46 cm^{-1} for second 3 hours of extraction. The peaks of 2927.94 cm^{-1} during 6 hours of extraction, at first 3 hours of extraction with 2955.93 cm^{-1}, 2925.27 cm^{-1} and for second 3 hours of extraction at 2921.39 cm^{-1} are due to CH stretching vibrations of CH, CH_2, CH_3 groups. The peaks of 2857.24 cm^{-1} and 2851.34 cm^{-1} for the first 3 hours and second 3 hours of extraction respectively shows the existence of aldehyde –(C-H). The stretching vibrations of C=O were attributed to peaks of 1735.42 cm^{-1}, 1738.80 cm^{-1} and 1739.42 in which for extraction time of 6 hours, first 3 hours and second 3 hours respectively. The medium strong peaks at 1649.91 cm^{-1} for second 3 hours of extraction is due to C=N stretching. The peaks of 1541.43 cm^{-1} for 6 hours of extraction, 1541.52 cm^{-1} for first 3 hours of extraction as well as 1541.49 cm^{-1} for second 3 hours of extraction are resulted from N-O stretching. As for the absorption bands around 1456.89 cm^{-1} and 1377.83 cm^{-1} for extraction time of 6 hours, 1456.87 cm^{-1} and 1377.38 cm^{-1} at first 3 hours of extraction and for second 3 hours of extraction at 1456.93 cm^{-1} and 1377.60 cm^{-1} were the characteristics of C=H bending. Meanwhile, the C-O of aliphatic acid groups has been attributed to peaks of 1216.98 cm^{-1} and 1216.96 cm^{-1} for 6 hours and first 3 hours of extraction respectively. The peak of 1161.66 cm^{-1} for second 3 hours of extraction is due to S=O stretching. In addition, the additional peaks of 719.40 cm^{-1} at second 3 hours of extraction can be assigned to C=C bending modes for aromatic compounds meanwhile for peak of 625.61 cm^{-1} at 6 hours of extraction is due to C-Br stretching. Furthermore, for the additional peaks presented for 6 hours of extraction which are at 568.78 cm^{-1}, 549.26 cm^{-1} and 529.69 cm^{-1} are due to C-I stretching.

IV. CONCLUSION

In this study, the main objectives have been achieved successfully. The first objective which is to determine the oil yield from Citrus Lemon peel by using solvent extraction method was conducted. There are 3 organic solvents has been chosen which are Acetone, Chloroform and n-Hexane. The highest percentage of oil yield was found to be by using Chloroform as a solvent with 30.6627%. The results were followed by Acetone and n-Hexane with percentage of oil yield 30.0613% and 27.4790% respectively. To complete the second objective which are to determine the component exist by using GCMS analysis as well as FTIR analysis to identify the functional group for oil of Citrus Lemon peel, the parameter that has been varied were the extraction time which are 6 hours, first 3 hours and second 3 hours. The GCMS analysis has shown positive results. Firstly, for the extraction of oil by using Chloroform as a solvent, there are three main components were found to be dominant which are Coumarin, α-Pinene and 7H-Furo(3,2-g) (1) benzopyran-7-one,9-hydroxy-. Coumarin was found to have the highest amount in each of extraction time that has been varied. Coumarin is the secondary metabolites that typically found in citrus plants where this component possesses variety of biological properties such as antioxidant, antimicrobial, anti-inflammatory and enzyme inhibitory activity. α-Pinene is the component which was found at 6 hours as well as second 3 hours of extraction time. This component is the most widely encountered terpenoid in nature where it is typically useful to treat the diseases such as arthritis, multiple sclerosis and Chron's. As for 7H-Furo(3,2-g) (1)

benzopyran-7-one,9-hydroxy- or commonly known as Psoralens (Furanocoumarins), it is the extra ring on the structure of coumarin. This component typically used to induce photochemical reactions in the skin. As by using Acetone as a solvent in extraction, the dominant main compound was Benzoic acid, 2,4-dihydroxy-3, 5,6-trimethyl-, methyl ester. This component is the natural fibers that typically produced by plant or animal and used in fragrance materials. Meanwhile by using n-Hexane as a solvent, the dominant component was found to be n-Hexadecanoic acid. The common name for this component is palmitic acid and it is widely used in industries such as personal care products and cosmetics. In addition, for FTIR analysis the differences between principal bands for 3 different extraction time that has been varied was performed by using data records. The functional groups present in the oil sample has been identified based on the different spectral information spread along the spectral range that has been selected.

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