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Extraction of Essential Aroma Compounds from Several Malodorous Indonesian Plants Using Simultaneous Steam Distillation-Extraction

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The research aim to extract and analyze composition and type of aroma compounds contained in essential oil from several malodorous Indonesian plants, namely noni fruits (*Morinda citrifolia* L.), jengkol beans (*Archidendron pauciflorum*), petai beans (*Parkia speciosa*) and sembukan leaves (*Paederia foetida* L.). Extraction was done by simultaneous steam distillation-extraction, using three different solvent, *n*-hexane, ethyl acetate and chloroform. The composition of essential aroma was determined by GC-MS. The results showed that ethyl octanoate and octanoic acid were the major component in noni fruits. 1,2,4-Trithiolane was found as major component in jengkol and petai beans. Isopropyl propanoate and 2,4-*bis*(1,1-dimethylethyl)phenol found as major component in sembukan leaves. This research showed that malodorous compound of noni fruits was fatty acid, while its of jengkol beans, petai beans and sembukan leaves was sulfur compounds. Solvents used influenced the composition of extracted aroma compounds significantly.

Keywords: Noni fruits, Petai beans, Jengkol beans, Sembukan leaves, Essential oil, Steam distillation-extraction, Malodor.

INTRODUCTION

Since the 1960s, Indonesia has been known as one of the biggest producers of essential oil in the world. Biologically, essential oil is the secondary metabolite that usually serves as self-defense in order to prevent animals (pests) from eating the plants or as agent to compete with other plants in survival. In general, essential oil is largely used in the cosmetic, food, perfume, pharmaceutical, health and even insecticide industries. In addition to aromatic essential oil, essential oil from malodorous plants is needed. Malodorous essential oils can be used as raw material for chemical weapons and to produce a flavourful foul specific scent on some certain foods.

Simultaneous steam distillation-extraction (SDE) has been known as one the methods to extract aroma from food material and was first introduced by S.T. Likens and G.B. Nickerson in 1964. In this method, sample was boiled under stirring in the flask at low temperature under the boiling point. Volatile components were then steam-distilled through the upper part of distillation tube, simultaneously, solvent vapours in another flask distilled through another distillation tube. Vapours condensed and the extraction process began between both on the condenser surface [1]. This method prevent volatile components from damaged. Steam distillation-extraction is common technique for quantitative extraction of volatile components [2-4]. Steam distillation-extraction was good in extraction of high-volatile components due to the amounts of the components extracted were greater compared with Soxhlet extraction and steam distillation-liquid liquid extraction (SD-LLE). This method also showed good in recovery and repeatability, hence this method was suitable for proper quantitative analysis [2,3].

Several malodorous Indonesian plants are noni fruits (*Morinda citrifolia* L.), jengkol beans (*Archidendron pauciflorum*), petai beans (*Parkia speciosa*) and sembukan leaves (*Paederia foetida* L.). These plants are commonly found in Indonesia and have been known as malodorous plants. Previous research has showed that octanoic acid and hexanoic acid were the major components in noni fruits essential oil along with other compounds such as decanoic acid, 3-methyl-3-buten-1-ol, methyl octanoate, ethyl octanoate [5-10]. Research in petai beans indicated that it contain sulphur-containing compounds where major compound was 1,2,4-trithiolane. Others sulphur-containing compounds such as 1,2,4,6-tetrathiepane, 1,2,4,5-tetrathiane, 1,2,3,5,6-pentathiepane (lenthionine) found in petai beans [11-13]. Meanwhile research related to sembukan leaves (*Paederia foetida* L.) showed that in its leaves contained linalol as major component. Leaves yielded sulphur-containing compounds in greater quantities than stems and flowers, namely dimethyl disulphide and dimethyl trisulphide, a volatile compounds that suggested responsible to its aroma constituents [14].

Research showed that essential oil was produced from similar plants from different regions and extracted with different methods, could yielded different composition. It was indicated that the composition of essential oil was influenced by environment [15,16] and extraction methods used [2,3,7,17]. Although the composition of essential oil of some malodorous plants has been known, but to date there has been no research on the composition of essential oil from Indonesia malodorous plants, more specifically from noni fruits, jengkol beans, petai beans and sembukan leaves. In this paper, we report the composition of essential oil from those malodorous plants obtained by steam distillation-extraction.

EXPERIMENTAL

Samples were noni fruits, jengkol beans, petai beans and sembukan leaves and other reagent was NaCl. Steam distillation-extraction was carried out as described elsewhere, consists of round-bottom flask, condenser, hose, hot plate and oil bath [18-20]. *n*-Hexane, ethyl acetate and chloroform were employed as solvent, respectively. Analytical scale and other qualitative and quantitative glasses were used for all experiments. Shimadzu QP 2010 ULTRA GC-MS was used for analysis.

General procedure

Sample preparation: Malodorous plant samples were cut into small, for samples from jengkol and petai beans, those skins were peeled before hand.

Essential oil extraction: For each extraction, noni fruit (500 g), jengkol beans (400 g), petai beans (350 g) and sembukan leaves (200 g), respectively and 70 g NaCl in 750 mL of distilled water were placed in a 2 L flask. Another flask was filled with 150 mL organic solvents (*n*-hexane, ethyl acetate, or chloroform). Samples were heated at 150 °C (in oil bath) and organic solvent was heated to its boiling point. Steam distillation was stopped after 2 h. Extracts were collected and solvent removed by evaporated.

Detection method: Components of essential oil compounds were analyzed by Shimaszu QP 2010 ULTRA GC-MS equipped with BD5 columns. Temperature was set at 60 °C for the columns, then raised to 280 °C at 8 °C/min. Analysis held for 27.5 min. Injection volume was 0.2 µL for each sample with pressure at 80.2 kpa, flow rate at 1.32 mL/min, split ratio of 200 and linear flow rate at 41.7 mL/min.

RESULTS AND DISCUSSION

Composition of noni fruits essential oil: The essential oil from noni fruits extracted by *n*-hexane showed 24 peaks, with ethyl octanoate as major component (40.88 %). Meanwhile, extracted by chloroform showed 27 peaks and 14 peaks extracted by ethyl acetate with octanoic acid as major component (61.91 and 74.96 %, respectively). Octanoic acid was the major volatile compound in noni fruits, this finding supports the previous reports [5-10]. In this research, ethyl octanoate identified as major component when *n*-hexane was used due to the polarity of *n*-hexane that could dissolve ethyl octanoate, which is non polar compound to organic phase. The most dominant components in noni fruits essential oil were fatty acids and esters. The composition of components presented in Table-1. Octanoic acid and hexanoic acid indicated responsible to foul-smell in noni fruits.

TABLE-1
COMPOSITION OF COMPONENTS IN NONI FRUITS ESSENTIAL OIL (%)

Compound	Solvent		
	n-Hexane	$CHCl_3$	EtOAc
Fatty acids			
Hexanoic acid	0.53	21.17	7.66
Octanoic acid	15.87	61.91	74.96
Butanoic acid	–	0.12	–
2-Methylbutanoic acid	–	0.12	–
3-(2-Hydroxyphenyl)-propanoic acid	–	0.12	–
Butyloctanoic acid	3.85	–	7.66
Esters			
Ethyl hexanoate	4.11	9.46	–
Methyl octanoate	5.27	2.28	5.52
Hexyl hexanoate	6.17	0.14	–
3-Methyl-butyl-2-en-octanoate	1.46	1.85	4.19
Hexyl octanoate	5.63	0.09	–
Methyl hexanoate	–	0.75	1.11
4-Pentenyl hexanoate	–	0.38	–
3-Methyl-2-butenyl hexanoate	–	0.11	0.66
Methyl decanoate	0.48	0.19	–
Ethyl octanoate	40.88	–	0.41
Isobutyl octanoate	0.86	–	4.05

Composition of jengkol and petai beans essential oil: The jengkol beans essential oil extracted by *n*-hexane showed 9 peaks, 18 peaks extracted by chloroform and 14 peaks extracted by ethyl acetate. 1,2,4-Trithiolane was identified as major component in those extraction with percentage 11.03, 52.02 and 64.07 %, respectively. The components of jengkol beans oil were dominated by sulphur-containing compounds. This compounds indicated responsible to foul-smell of jengkol beans. In addition, jengkol beans oil also contained aromatic compounds, esters, alcohols, alkanes, terpenes and alkenes. Composition of sulphur-containing compounds in jengkol beans oil is presented in Table-2.

Chromatogram of petai beans essential oil extracted by *n*-hexane is presented in Fig. 1. Chromatogram showed 7 peaks, with 1,2,4-trithiolane as major component (27.22 %). Meanwhile, identification of petai beans oil extracted by chloroform showed 15 peaks and 11 peaks extracted by ethyl acetate. Both of that showed 1,2,4-trithiolane as major component with percentage 78.54 and 87.7 %, respectively. This finding supports the previous report in accordance with Gmelin *et al.* [11] and Frerot *et al.* [13]. The major component of petai beans oil was sulphur-containing compounds. It was indicated responsible to foul-smell of petai beans. Lenthionine was well known in petai and its also contained in shitake mushroom along with 1,2,4,5-tetrathiane [21-23]. Sulphur-containing compounds present in petai beans oil have the same arrangement of sulphur and carbon atoms (S-CH-S) [13]. The composition of components in petai beans essential oils presented in Table-2.

Composition of sembukan leaves essential oil: Sembukan leaves essential oil extracted by *n*-hexane has no components identified. It was suggested that the polarity of compounds in sembukan leaves has no similarity to its of *n*-hexane, hence could not be extracted. Identification of sembukan leaves oil

TABLE-2
COMPOSITION OF SULPHUR-CONTAINING COMPOUNDS IN JENGKOL AND PETAI BEANS ESSENTIAL OILS (%)

Compound	Jengkol beans			Petai beans		
	n-Hexane	$CHCl_3$	EtOAc	*n*-Hexane	$CHCl_3$	EtOAc
1,2,4-Trithiolane	11.03	52.02	64.07	27.22	78.54	87.77
1,3,5-Trithiane	0.51	9.01	2.89	6.32	6.29	2.35
1,2,4,5,7-Pentathioctane	1.98	23.94	20.29	–	8.21	–
3,5-Dimethyl-1,2,4-trithiolane	–	2.27	3.16	–	–	–
Tris(methylthio)-methane	–	0.44	0.62	–	–	–
1,2,4,5-Tetrathiane	–	3.01	0.46	–	0.65	0.60
1,2,5,6-Tetrathioctane	–	3.69	0.79	–	0.30	–
1,1-[(Methylthio)-methylen]-ethane	–	0.31	–	–	–	–
1,2,4,6-Tetrathioptane	–	–	–	0.56	–	5.00
1,2,3,5-Tetrathiane	–	–	–	–	1.25	1.44
Lenthionine	–	–	–	–	0.33	0.35

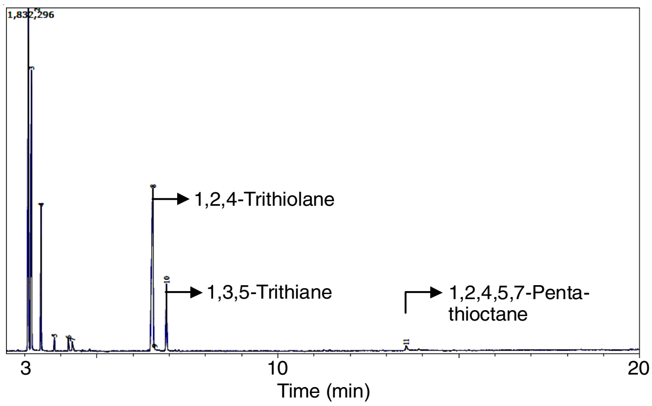

Fig. 1. Chromatogram of petai beans essential oil extracted by *n*-hexane

extracted by chloroform indicated 19 peaks, with 2,4-*bis*(1,1-dimethyl ethyl)-phenol as major component, while extracted by ethyl acetate showed 7 peaks, with isopropyl propanoate (33.78 %) as major component along with sulphur-containing compounds, alcohols, aromatic compounds, alkanes, alkenes and terpenes. Although the major component of sembukan leaves oil belong to esters group, sulphur-containing compounds that contained in its indicated responsible in producing foul-smell of sembukan leaves [14]. Sulphur-containing compounds contained in sembukan leaves oil is presented in Table-3.

TABLE-3
COMPOSITION OF SULPHUR-CONTAINING COMPOUNDS IN SEMBUKAN LEAVES ESSENTIAL OIL (%)

Compound	Solvent		
	n-Hexane	$CHCl_3$	EtOAc
Dimethyl disulfide	–	10.06	6.51
1,2,4-Trithiolane	–	10.24	14.58
Dimethyl trisulfide	–	2.42	–

Effect of solvent on composition of essential oil: Based on this research, chloroform could extracted compounds greater for each samples than other solvents. The number of compounds extracted by each solvents presented in Table-4. Polarity of *n*-hexane, chloroform and ethyl acetate decreased due to dielectric constants, 2.0, 4.8 and 6.0, respectively. Chloroform could extracted more components than ethyl acetate, chloroform and *n*-hexane could. It might due to the polarity of chloroform where it is semi-polar, hence could extracted some polar and non-polar components. Ethyl acetate has high polarity than others, hence only extracted the polar components and *n*-hexane was the lowest one, extracted the non-polar components. Noni fruits contained more non-polar and semi polar compounds due to the previous report [5-10], therefore chloroform and *n*-hexane could extracted better than ethyl acetate. Differ from jengkol beans, petai beans and sembukan leaves, those contained more polar compounds due to the sulphur-containing compounds [10-14], hence chloroform and ethyl acetate performed better extraction than *n*-hexane.

TABLE-4
NUMBER OF COMPOUNDS EXTRACTED BY EACH SOLVENTS

Compound	Solvent		
	n-Hexane	$CHCl_3$	EtOAc
Noni fruits	19	21	10
Jengkol beans	7	14	11
Petai beans	9	13	9
Sembukan leaves	–	17	6

Identification of malodorous compounds: Several plants with foul-smell contained many compounds that responsible to its smell, according to the literature, those are categorized into malodorous compounds. The malodorous compounds in the extracted essential oils are presented in Table-5.

The data indicated that the foul-smell produced by several compounds contained in each of samples. For example, in jengkol beans there were 8 compounds identified as malodorous compounds. Hexanoic acid, octanoic acid and butanoic acid were succesfully extracted from noni fruits and it was suggested responsible in producing the malodorous aroma of the fruits, since those were not identified in the other malodorous plants. 1,2,4-Trithiolane and dimethyl disulfide were found in sembukan leaves, specifically compound indicated responsible in producing the malodorous aroma of the leaves was dimethyl disulfide, since 1,2,4-trithiolane also found in jengkol and petai beans. Compounds that responsible in producing malodorous aroma in petai beans were 1,2,4-trithiolane, 1,3,5-trithiane, 1,2,4,6-tetrathieptane, 1,2,4,5,7-pentathioctane, 1,2,5,6-tetrathioctane, 1,2,4,5-tetrathiane, 1,2,3,5-tetrathiane and lenthionine. The malodorous aroma of petai beans might caused by dimethyl trisulfide, since the other compounds were identified in sembukan leaves and jengkol beans. The most responsible in producing malodorous aroma of jengkol beans were 1,2,4-trithiolane, 1,3,5-trithiane, 1,2,4,5,7-pentatioctane,

TABLE-5
COMPONENT OF MALODOROUS COMPOUNDS IN THE ESSENTIAL OIL OF SAMPLES

Malodorous compound	Noni fruits	Sembukan leaves	Petai beans	Jengkol beans
Octanoic acid	✓	–	–	–
Hexanoic acid	✓	–	–	–
Butanoic acid	✓	–	–	–
Dimethyl disulfide	–	✓	–	–
1,2,4-Trithiolane	–	✓	✓	✓
Dimethyl trisulfide	–	–	✓	–
1,3,5-Trithiane	–	–	✓	✓
1,2,4,6-Tetrathioptane	–	–	✓	
1,2,4,5,7-Pentathioctane	–	–	✓	✓
1,2,5,6-Tetrathioctane	–	–	✓	✓
1,2,4,5-Tetrathiane	–	–	✓	✓
1,2,3,5-Tetrathiane	–	–	✓	–
Lentionine	–	–	✓	-
3,5-Dimethyl-1,2,4-trithiolane	–	–	–	✓
Tris(methylthio) methane	–	–	–	✓
1,1-[(Methylthio)methylen]ethane	–	–	–	✓

3,5-dimethyl-1,2,4-trithiolane, *tris*(methylthio)methane, 1,2,4,5-tetrathiane, 1,2,5,6-tetrathioctane and 1,1-[(methylthio)-methylen]ethane. However, compounds that produced malodorous aroma for jengkol beans were 3,5-dimethyl-1,2,4-trithiolane, *tris*(methyltiho) methane and 1,1-[(methylthio)-methylene]ethane.

From the findings described, steam distillation-extraction method as introduced by Likens-Nickerson was successfully to extract the compounds contained in essential oil from malodorous plants. However, the success of the extraction was determined by using an appropriate solvent.

Conclusion

It could be concluded that the major component in noni fruits essential oil extracted by *n*-hexane was ethyl octanoic, while extracted by chloroform and ethyl acetate found octanoic acid as major component. The essential oil from jengkol beans and petai beans extracted by *n*-hexane, chloroform and ethyl acetate showed 1,2,4 trithiolane as the major component. Sembukan leaves essential oil extracted by ethyl acetate showed isopropyl propanoate and 2,4-*bis*(1,1-dimethylethyl) phenol as major component if extraction was done by chloroform, while extracted by *n*-hexane showed nothing. The malodorous compound of noni fruits was fatty acids and the malodorous compounds of jengkol beans, petai beans and sembukan leaves were sulphur-containing compounds. Solvent used during extraction affect the composition of the essential oil extracted significantly. Chloroform extracted more appropriate compared to other solvents.

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